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2,2-Dihydroperfluoropentane (HFC 4310 mf) synthesis from HFP dimer

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Abstract

The thermodynamic dimer of hexafluoropropene (HFP) may be used for the one pot synthesis of 2H-perfluoro-2-pentene, which is the starting compound for preparation of 2,2-dihydroperfluoropentane (HFC 4310 mf).

Keywords: Hexafluoropropene dimer; Perfluoroisobutene; HFC 4310 mf; HFC 236 fa

1. Introduction

Reactions of perfluoro(2-methyl-2-pentene) (**1**), the thermodynamic dimer of hexafluoropropene (HFP), are sometimes impossible to explain without invoking isomerization to terminally unsaturated perfluoro(2-methyl-1-pentene) (**2**) [1–3]. One well-known incidence of such isomerization is evident in the structure of thermodynamic HFP trimer. It contains a normal propyl group (instead of isopropyl), which is derived from the isomeric dimer **2** with the terminal double bond [4] (Scheme 1).

Methylpentene (**2**) is a homolog of perfluoroisobutene (PFIB) $CF_2{=}C(CF_3)CF_3$ and we anticipated its high reactivity in nucleophilic additions like those of PFIB, the chemistry of which is very well-known (see review [5]). PFIB is a highly toxic gas resulting from processes where perfluorinated compounds are exposed to high temperature. PFIB is highly electrophilic and reacts with water to give 2H-hexafluoroisobutyric acid [6] and 2,2-dihydrohexafluoropropane (HFC 236 fa) as a result of decarboxylation of this acid [7] (Scheme 2).

2,2-Dihydrohexafluoropropane may be also prepared from the adduct of PFIB with methanol [8,9], which has been a byproduct of some industrial processes.

We decided to reinvestigate the reaction of the HFP dimer with water and alcohols. In this case, one might expect to obtain 2,2-dihydrodecafluoropentane (HFC 4310 mf), which is known as a good candidate for replacing CFC 113 [10].

2. Results and discussion

Hoechst AG chemists in 1976 [11] first studied the reaction of HFP dimer **1** with water in the presence of triethylamine. They found that water reacted easily to substitute the vinylic fluorine, forming triethylammonium perfluoro(2-methyl-2-pentene-2-olate) (Scheme 3).

Three years later, Nesmeyanov Institute chemists showed that the reaction of this enolate with additional triethylamine and water gives 2H-nonafluoro-2-pentene (**3**). This resulted from enol rearrangement to the unsaturated acid fluoride and subsequent substitution of COF group by hydrogen [12] (Scheme 4).

We tried to combine both these reactions by reacting **1** with water and a two-fold excess of triethylamine to hopes of preparing olefin **3**. However, pentafluorobutanone (**5**) and hexafluoropropane (**6**) were the main reaction products with only a small amount (12% yield) of olefin **3**. The intermediate 2H-perfluoroisopropylpentafluoroethyl ketone (**4**) or its triethylammonium enolate undergoes mainly haloform degradation and hydrolysis, rather than rearrangement (Scheme 5).

Water, being a small molecule, attacks the vinylic fluorine in the HFP dimer very easily, and we could not find conditions where the isomer with a terminal double bond is the preferred reacting species.

The situation is different when bulky *tert*-butanol is used in place of water (see also [13]). The primary reaction product, unstable 2H-perfluoro(2-methylpentyl)-*tert*-butyl ether (**7**), may be isolated if pyridine is used as the catalyst. A substantial amount of ester **8** is also produced, probably

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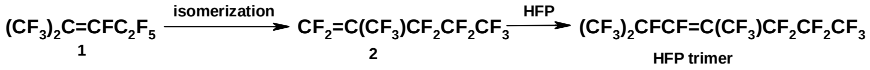
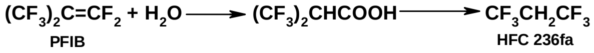
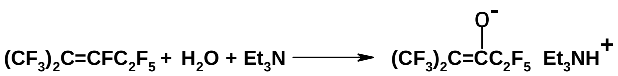


Scheme 1.



Scheme 2.



Scheme 3.

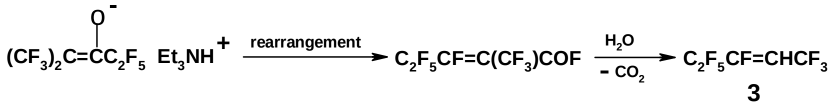
through the elimination of *tert*-butylfluoride, followed by the reaction of the resulting 2H-perfluoro(2-methylpentanoic) acid fluoride with *tert*-butanol. In this particular case, as in other reactions of the dimer **1** with water and *tert*-butanol, some quantity of hydrogen fluoride is produced in the form of its complex with tertiary amines. This HF is captured by the HFP dimer to give 2H-perfluoro(2-methylpentane) $(CF_3)_2CHC_3F_7$, which decreases the yield of the desired ether **7** or esters **8** and **9**. This is not a real loss, because the methylpentane C_6HF_{13} may be successfully used in the synthesis of pentene **3** instead of HFP dimer (see Section 3.8 for experimental details).

With triethylamine, the α-difluoroether (**7**) is easily (even spontaneously) transformed into fluorinated 2-methylpentanoic (**8**) and 2-methylpentenoic (**9**) acid esters (Scheme 6).

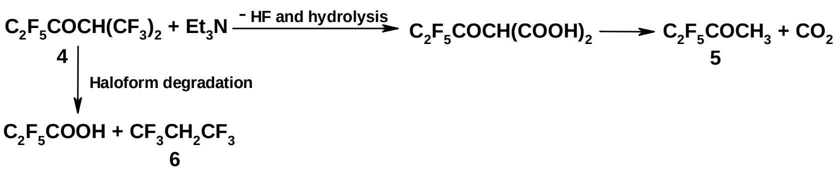
A mixture of acids **10** and **11** was prepared from esters **8** and **9** by heating with *p*-toluenesulfonic acid. This acid mixture undergoes decarboxylation in aqueous solution in the presence of triethylamine. A sample of this mixture with approximately 40% of acid **10** was decarboxylated in this way and only C_5HF_9 pentene was obtained. There was none of the desired $C_5H_2F_{10}$ in the reaction product.

Decarboxylation of 2H-hexafluoroisobutyric acid (**12**) (prepared from PFIB) thus differs from decarboxylation of 2H-perfluoro(2-methylpentanoic) acid (**10**) (as a mixture with the acid **11** prepared from HFP dimer). Only alkane **6** was obtained from PFIB. Only olefin **3** was obtained from its C6 homolog (Scheme 7).

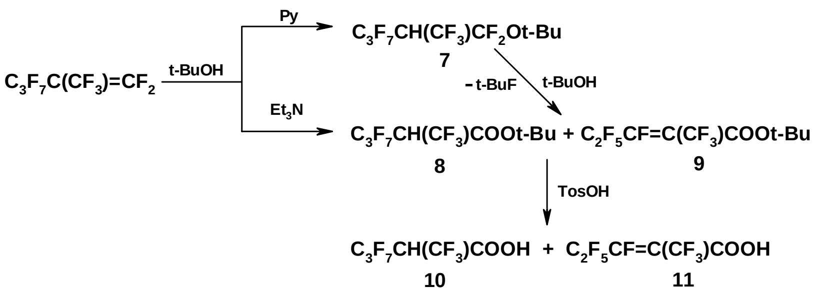
Preparation of 2H-pentafluoropropene (**13**) from hexafluoroisobutyric acid is rather difficult. Tertiary amines do not work, and thermal decarboxylation of the Na or K salts of the acid requires exceptionally dry conditions [14]. In contrast, the 2H-nonafluoropentene (**3**), and not the pentane (HFC 4310 mf), is the only product from decarboxylation of



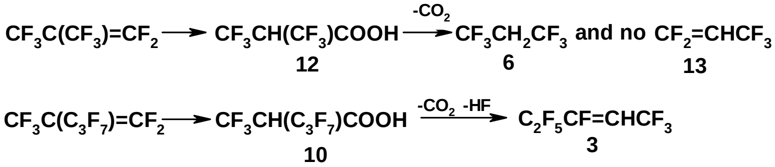
Scheme 4.



Scheme 5.



Scheme 6.



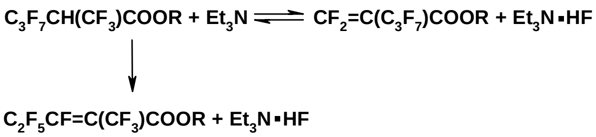
$$CF_3C(CF_3)=CF_2 \rightarrow \underset{\mathbf{12}}{CF_3CH(CF_3)COOH} \xrightarrow{-CO_2} \underset{\mathbf{6}}{CF_3CH_2CF_3} \text{ and no } \underset{\mathbf{13}}{CF_2=CHCF_3}$$

$$CF_3C(C_3F_7)=CF_2 \rightarrow \underset{\mathbf{10}}{CF_3CH(C_3F_7)COOH} \xrightarrow{-CO_2\ -HF} \underset{\mathbf{3}}{C_2F_5CF=CHCF_3}$$

Scheme 7.

$$CF_3CH(CF_3)COOR + Et_3N \rightleftharpoons CF_2=C(CF_3)COOR + Et_3N\cdot HF$$

Scheme 8.



$$\begin{tikzcd} C_3F_7CH(CF_3)COOR + Et_3N \arrow[r, phantom, "\rightleftharpoons"] \arrow[d] & CF_2=C(C_3F_7)COOR + Et_3N\cdot HF \\ C_2F_5CF=C(CF_3)COOR + Et_3N\cdot HF & \end{tikzcd}$$

Scheme 9.

the acid **10** in aqueous solution. The same difference is observed when neat esters of the both acids are treated with base. There is no visible reaction of 2H-hexafluoroisobutyric acid methyl or ethyl ester with triethylamine, but we observed immediate dehydrofluorination in case of ester **8**. The explanation for the difference may be as follows: dehydrofluorination of a hexafluoroisobutyrate is a reversible process because a very reactive terminal double bond formed in the reaction (Scheme 8).

The same reversible process is possible for 2H-perfluoro-2-methylpentanoic acid ester, but much less active internal double bond can also be formed, rendering dehydrofluorination irreversible (Scheme 9).

The synthesis of 2H-nonafluoropentene (**3**) from HFP dimer may be accomplished as a one pot preparation (see Section 3). The target compound $C_3F_7CH_2CF_3$ (HFC 4310 mf) was prepared by HF addition to the pentene **3** using Olah's reagent as a source of hydrogen fluoride or antimony pentafluoride as a catalyst in anhydrous HF solution.

3. Experimental details

Specialty Materials Manufacturing Division analytical group at 3 M provided analytical data. The ^1H and ^{19}F NMR spectra were acquired using a Bruker AC 270 spectrometer operating at 270.13 or 254.18 MHz frequency. The samples were placed in an NMR tube, spiked with small amount $CFCl_3$ and TMS for both ^{19}F and ^1H chemical shifts zero reference given in ppm, and spiked with small amount of *p*-hexafluoroxylene (*p*-HFX) for use as a cross integration standard. Use of the *p*-HFX facilitates the cross correlation of various proton and fluorine signals intensities for qualitative purposes [15]. The cross integration measurement technique was used to derive the overall relative mole and weight percent concentrations for all the identified components. $CFCl_3$ was the solvent for ^{19}F as well as for ^1H NMR, unless otherwise noted. For analysis of acids **10** and **11** Varian UNITY plus 400 and Varian UNITY INOVA 500 FT-NMR spectrometer were used. Initial one-dimensional (1D) 400 MHz ^1H NMR and 376 MHz ^{19}F NMR were acquired. Additional two-dimensional correlated spectroscopy (2D-COSY) experiments were also performed to facilitate assignment of some of the impurity components. Specifically, a $^{19}F/^{19}F$ NMR homonuclear COSY experiment and a $^{19}F/^1H$ NMR heteronuclear HF-COSY experiment were collected. GC/MS analyses were accomplished using a 105 m × 0.32 mm Rtx-5 column to introduce the sample into the Finnigan SSQ-700 mass spectrometer. The sample components were ionized using chemical ionization with methane as the reagent gas. The GC column was operated from 40 to 300 °C with a temperature ramp of 10°/min. With the aid of GC/MS analysis results, the combined 1D and 2D ^1H NMR spectral data were used to assign the major component as the *E*-isomeric form of the acid **11**. Two of the other components including the *Z*-isomeric form and acid **10** were also assigned. The 1D ^{19}F NMR spectrum was then used to calculate the relative weight percent concentrations of the three identified components. A gas chromatograph HP 5890 Series 2 with J&W Scientific fused silica capillary column DB 210 (30 m × 0.325 mm) with a FID detector was used for both liquids and gases analysis. IR spectra were recorded on Digilab FTS-40 FTIR spectrometer. Some well-known non-fluorinated compounds like isobutene, *tert*-butanol, etc. were identified by comparison of their GC retention time with the Aldrich samples.

3.1. Reaction of HFP dimer with water and triethylamine

HFP dimer **1** (3.0 g, 10 mmol), triethylamine (3.03 g, 30 mmol), 3 ml H_2O and 1.7 g CH_3CN were heated in an Ace-Glass Inc. pressure tube with stirring at 45–60 °C for 5 h. The cooled (−15 °C) reactor was opened and the reaction mixture was distilled to give 0.96 g liquid with bp up to 70 °C and 0.74 g of low boiling material in a trap (−78 °C). The combined liquid was cooled to 0 °C and washed with 15% HCl solution, and the organic layer was separated by water freezing to get 1.4 g of the mixture (GC): 47% hexafluoropropane (**6**) (43% yield), 22% nonafluoropentene (**3**) (12% yield) and 18% pentafluorobutanone (**5**) (18% yield) (see NMR and MS in Section 3.7).

3.2. Reaction of HFP dimer with tert-butanol and triethylamine

HFP dimer perfluoro(2-methyl-2-pentene) (6.0 g, 20 mmol), triethylamine (2.05 g, 20 mmol) and *tert*-butanol (3.7 g, 50 mmol) were heated in an Ace-Glass Inc. pressure tube with Ace-Thred PTFE cap and with a magnetic bar stirrer at 55–60 °C for 23 h. The initially clear liquid became a suspension of white crystals in a slightly colored solution. The tube was cooled to 0 °C, opened and water (5 ml) was added to dissolve the solid material. The lower organic layer washed with 15% HCl solution and water, dried $MgSO_4$ to give 9.69 g of a mixture consisting of (GC): 14% isobutene, 1% *tert*-butanol, 14% *tert*-butyl fluoride $(CH_3)_3CF$ ^{19}F and ^1H NMR: −132.4 (CF dectet), 1.27 (CH_3 d); MS: no M^+ was observed, 61 [$(M-CH_3)^+$ 7], 57 [$(M-F)^+$ 100]; 4% 2H-perfluoro(2-methylpentane) $(CF_3{}^a)_2CHCF_2{}^bCF_2{}^cCF_3{}^d$ ^{19}F and ^1H NMR: −62.1 (a, CF_3 m), −112.4 (b, CF_2 m), −125.9 (c, CF_2 dm), −80.9 (d, CF_3 t), 3.80 (CH m); MS: no M^+ was observed, 301 [$(M-F)^+$ 100]; 17% ester **9** $CF_3{}^aCF_2{}^bCF^c{=}C(CF_3{}^d)COOC(CH_3{}^e)_3$ ^{19}F and ^1H NMR: −83.6 (a, CF_3 d), −120.2 (b, CF_2 d), −117.4 (c, CF m), −60.5 (d, CF_3 d), 1.45 (e, CH_3 s); MS: 333 [$(M+1)^+$ 5], 317 (10), 277 (100), 259 (88); 37% *tert*-butyl ester **8** $CF_3{}^aCF_2{}^bCF_2{}^cCH^e(CF_3{}^d)COOC(CH_3{}^f)_3$ ^{19}F and ^1H NMR: −80.86 (a, CF_3 t), −125.7 (b, CF_2 m), −113.5 and −115.8 (c, CF_2 Abq, $J = 285$ Hz), −62.9 (d, CF_3 m), 3.82 (e, CH m), 1.45 (f, CH_3 s); MS: 353 [$(M+1)^+$ 2], 325 (8), 297 (100), 279 (18). The mixture was distilled to give 6.87 g of a fraction with bp 120–135 °C ([6] bp 70–85 °C at 150 mmHg) consisted of (GC): 32% ester **9** and 29% ester **8** with the combined yield 88%.

3.3. Reaction HFP dimer with tert-butanol and pyridine

The same apparatus and procedure were used as in Section 3.2 employing 6.0 g (20 mmol) HFP dimer, 3.2 g (43 mmol) *tert*-butanol and 3.2 g (40 mmol) pyridine. After the reaction was completed, an excess of pyridine was washed out with water to give 6.2 g of organic material, which after distillation with water gave 2.9 g (36% yield) 2H-perfluoro(2-methylpentane) with bp 55–65 °C (79% pure) and 2.94 g of fraction with bp up to 101 °C consisting of (GC): 39% *tert*-butyl ester **8** and 49% *tert*-butyl ether (**7**) $CF_3{}^aCF_2{}^bCF_2{}^cCH(CF_3{}^d)CF_2{}^eOC(CH_3)_3$ ^{19}F and ^1H NMR: −80.97 (a, CF_3 t), −125.3 (b, CF_2 m), −111.2 and −112.3 (c, CF_2 Abq, $J = 300$ Hz), −61.7 (d, CF_3 m), −58.2 (e, CF_2 s broad), 3.60 (CH m), 1.40 (CH_3 s); MS: 373 [$(M-1)^+$ 10], 359 (100), 301 (14).

3.4. Dehydrofluorination of 2H-perfluoro(2-methylpentanoic) acid tert-butyl ester 8

By KOH: *tert*-Butyl esters **8** and **9** mixture (2.16 g) from Section 3.2 (41% for **8** and 40% for **9**) was refluxed with 10 ml 15% KOH solution. The two layers mixture did not visually change. There was separated 1.71 g (99% yield) liquid product which was pure (98.5% by GC) *tert*-butyl ester **9** of perfluoro(2-methyl-2-pentenoic) acid (two isomers 16:1).

By Et_3N: From 0.865 g of the esters mixture (74% of saturated ester **8** and 23% of unsaturated ester **9**) and 0.27 g (50% excess) triethylamine for 30 min at 20 °C (after washing with water and drying) there was prepared 0.782 g (87% yield) of the ester **9** with 92% (GC) purity.

3.5. Perfluoro(2-methyl-2-pentanoic) acid (10) and perfluoro(2-methyl-2-pentenoic) acid (11)

The above mixture of *tert*-butyl esters **8** and **9** (1.2 g) was heated with 0.17 g of Aldrich *p*-toluenesulfonic acid monohydrate at 150 °C for 30 min. The resulting water-insoluble mixture of acids **10** and **11** was dissolved in potassium bicarbonate solution, separated after acidification and distilled from the mixture with equal volume of conc. H_2SO_4 to give 0.8 g (80%) acids **10** and **11** with bp 135–137 °C, consisting of: 6.3% acid **10** $CF_3{}^aCF_2{}^bCF_2{}^cCH(CF_3{}^d)COOH$ ^{19}F and ^1H NMR: −80.6 (a, CF_3 t), −125.4 ($CF_2{}^b$ m), −113.2 and −114.6 (c, CF_2 Abq, $J = 284$ Hz), −62.7 (d, CF_3 m), 4.40 (CH qt or tq); acid **11** $CF_3{}^aCF_2{}^bCF^c{=}C(CF_3{}^d)COOH$ ^{19}F and ^1H NMR: 87.4% *E*-isomer (F^c *trans* $CF_3{}^d$), −83.3 (a, CF_3 d), −119.9 (b, CF_2 d), −110.8 (c, CF m), −60.0 (d, CF_3 d); 6.3% *Z*-isomer (F^c *cis* $CF_3{}^d$), −83.3(a, CF_3), −119.0 (b, CF_2 m), −104.0 (c, CF m) −56.0 (d, CF_3 m); acid **11** MS: 277 [$(M+1)^+$ 100], 259 (36), 237 (96) 213 (40); IR (neat, KBr, cm^{-1}): 1709 (C=C), 1743 (CO), 2800–3300 (OH).

3.6. 2H-perfluoro-2-pentene (3)

The solution of 2.97 g (11 mmol) acid **11**, 5 ml H_2O and 1.5 g (15 mmol) triethylamine was heated at 64–80 °C until a gas evolution was ceased. Combined organic material from a receiver and a trap (−78 °C) was washed by 15% HCl solution, then water, dried $MgSO_4$ and distilled to give 1.88 g (8 mmol, 73% yield) pentene **3** with bp 32–33 °C and purity (GC) 99% ([16] bp 32–33 °C). See NMR and MS in Section 3.7.

3.7. One pot synthesis 2H-perfluoro-2-pentene (3) from HFP dimer

The dimer **1** (400 g, 1.3 mol), triethylamine (170 g, 1.7 mol) and *tert*-butanol (224 g, 3 mol) were heated in a glass pressure reactor at 55–60 °C for 20 h with stirring. The reactor was cooled to 0 °C and opened (there was no pressure inside) and the reaction mixture washed by water, 15% HCl solution and water again to give 484 g organic material consisting of (GC): 71% mixture of esters **8** and **9** along with some low boiling compounds (same as in Section 3.2). The mixture was heated at 110–115 °C for 3 h with 15 g *p*-toluenesulfonic acid (TosOH) to give 365 g of crude acid mixture. To this acid mixture 300 ml H_2O was added and then gradually 150 g of triethylamine to keep the temperature below 65 °C. Decarboxylation started at 70 °C and the product with bp 65 °C was distilled and collected in a receiver and a trap (−78 °C). The combined distillate washed by 15% HCl solution, then water, dried $MgSO_4$ and redistilled to give 199.6 g (63%) of two isomeric (Z:E = 11:87) 2-hydroperfluoro-2-pentenes with bp 31–33 °C and purity 98%; $CF_3{}^aCH{=}CF^bCF_2{}^cCF_3{}^d$ ^{19}F and ^1H NMR: E-isomer, −60.2 (a, CF_3 dd), −113.3 (b, CF m), −123.3 (c, CF_2 dm), −84.4 (d, CF_3 dm), 5.81 (CH dq); Z-isomer (same designation), −55.8 (a, CF_3 m), −110.2 (b, CF m), −120.6 (c, CF_2 p), −82.9 (d, CF_3 s), 6.08 (CH dq); MS: 232 (M^+, 8), 213 (100), 163 (50), 113 (32). The pentene contains less than 2% pentafluorobutanone (**5**) as an impurity, $CF_3CF_2COCH_3$ ^{19}F and ^1H NMR: −82.9 (CF_3 s), −123.9 (CF_2 s), 2.3 (CH_3 s); MS: 163 [$(M+1)^+$ 100], 143 (5).

*3.8. Pentene **3** synthesis from 2H-perfluoro(2-methylpentane)*

The same procedure was used as in Section 3.7. From 6.4 g (20 mmol) C_6HF_{13} 5.08 g (50 mmol) triethylamine and 3.7 g (50 mmol) *tert*-butanol there was obtained 7.83 g organic material consisting of (GC): 14% i-C_4H_8, 19% *tert*-C_4H_9F, 2% starting C_6HF_{13}, 15% ester **8** and 42% ester **9**. This mixture and 0.45 g TosOH were heated at 115 °C for 3 h in a slow flow of nitrogen and in a trap (−78 °C) was collected 1.66 g of low boiling material including C_6HF_{13}. To 5.71 g of the residue was added 6 ml H_2O and 2.5 g triethylamine and the crude pentene was distilled out. It was washed, dried and redistilled to give 2.62 g (57%) of pentene **3** with bp 31–33 °C and purity 98%. The product contained 2% ketone **5**.

3.9. 2,2-Dihydrodecafluoropentane (HFC 4310 mf)

In a stainless steel tube a mixture of 5.0 g pentene **3** (GC purity 98%), 2.0 g Aldrich pyridinium poly(hydrogen fluoride) and 1.6 g acetonitrile was heated at 280 °C for 17 h. The reaction product was poured into ice water, the organic layer (4.3 g) was separated and distilled from the mixture with equal volume of conc. H_2SO_4 to give 3.79 g product with a bp 42–47 °C ([10] bp 46–47 °C) and consisting of (GC) 13% pentene **3** and 81% 2,2-dihydroperfluoropentane $CF_3{}^aCH_2CF_2{}^bCF_2{}^cCF_3{}^d$ ^{19}F and ^1H NMR ($CDCl_3$): −61.6 (a, CF_3 pt), −115.2 (b, CF_2 m), −128.3 (c, CF_2 s), −81.0 (d, CF_3 t), 2.94 (CH_2 m); MS: no M^+ was observed, 233 [$(M-F)^+$ 100], 213 (10), 163 (2). The product yield was 58%.

In another experiment, 19.0 g pentene **3** and 8.1 g 10% solution of SbF_5 in anhydrous HF were heated in a stainless steel tube at 240 °C for 20 h to give 15.3 g of the HFC 4310 mf with bp 46–47 °C and purity 96%. The yield was 71%.

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