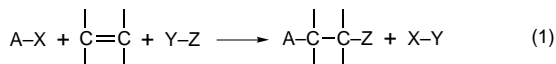# Conjugate Electrophilic Iodofluorination of Fluoroolefins†

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Conjugate electrophilic addition to a double bond of an olefin is a process in which two fragments of halogen fluoride, not connected to each other in the starting material, are added across the double bond:[1]

$$A{-}X + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} + Y{-}Z \longrightarrow A{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}Z + X{-}Y \qquad (1)$$

Many such reactions are known and are summarized in several reviews.[1−3] In the addition of halogen fluoride across a hydrocarbon double bond, a typical reagent combination includes an *N*-halogen compound (*N*-halosuccinimides or hexachloromelamine) and anhydrous HF (AHF) or another source of HF, such as the complex HF/pyridine.[4,5] Addition of halogen fluorides across the electron poor double bond of fluoroolefins is generally carried out using more powerful electrophiles, such as ClF^2 or a combination of BrF_3/Br_2^{6-8} or $IF_5/I_2^{6,9}$ as a "stochiometric equivalent"[2] of BrF or IF.

Recently it was found that the solution of an *N*-halo compound in a superacid such as $HOSO_2F$ is an effective reagent for conjugate addition of the elements X^+ and OSO_2F^- (X = Cl, Br) across the double bond of terminal fluoroolefins.[10] Although this reaction does not involve the formation of halogen fluorosulfate as an intermediate, it is a good alternative route for the preparation of corresponding fluorosulfates, otherwise only available by addition of stable but potentially hazardous hypohalites ($XOSO_2F$) to fluoroolefins.[11]

The combination of X_2/protic acid (HF^2 or $HOSO_2F^{12}$) is usually not effective for this reaction, although it was reported that iodine in the presence of certain oxidizing agents in AHF is efficent for the synthesis of C_2F_5I and *i*-C_3F_7I at 140−160 °C.[13,14]

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(1) German, L. S.; Knunyants, I. L. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 349.

(2) Bogouslavskaya, L. S.; Chuvatkin, N. N. In *New Fluorinating Agents in Organic Synthesis*; German, L. S., Zemskov, S., Eds.; Springer-Verlag: New York, 1989; pp 140−196, review on application of halogen fluorides in organic synthesis.

(3) Belen'kii, G. G.; German, L. S. In *Chemistry Reviews, Section B*; Vol'pin, M. E., Ed.; Soviet Scientific Reviews; Harwood Academic Publishers GmbH: New York, 1984; pp 183−218.

(4) Olah, G.; Nojima, M.; Kekekas, I. *Synthesis* **1973**, 779.

(5) Hamman, S.; Beguin, C. G. *J. Fluorine Chem.* **1979**, *13*, 163.

(6) Chambers, R. D.; Musgrave, W. K. R.; Savory, J. *J. Chem. Soc.* **1961**, 3779.

(7) Yuminov, V. S.; Pushkina, L. N.; Sokolov, S. V. *Zh. Obsh. Khim.* **1967**, *37*, 375.

(8) Lo, E. S.; Readio, J. D.; Iserson, H. *J. Org. Chem.* **1970**, *35*, 2051.

(9) Hauptschein, M.; Braid, M. *J. Am. Chem. Soc.* **1961**, *83*, 2383.

(10) German, L. S.; Savicheva, G. I. *Izv. Akad. Nauk SSSR Ser. Khim.* **1984**, 479.

(11) Fokin, A. V.; Studnev, Yu. N. In *Chemistry Reviews, Section B*; Vol'pin, M. E., Ed.; Soviet Scientific Reviews; Harwood Academic Publishers GmbH: New York, 1984; pp 47−96.

(12) Fokin, A. V.; Studnev, Yu. N.; Rapkin, A. I.; Krotovich, I. N.; Tamarinov, A. S.; Verinikin, O. V. *Izv. Akad. Nauk SSSR Ser. Khim.* **1985**, 2298.

In the search for an alternative route to the important intermediates for many fluorochemicals, perfluoroalkyl iodides,[15] a new process for the preparation of R_fI has been discovered. This paper presents the results of the reaction of fluoroolefins with solutions of the readily available iodine monochloride in AHF.
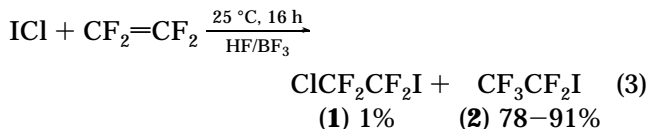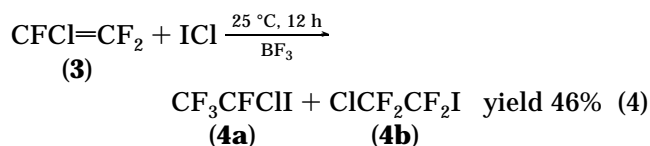
Results and Discussion

The reactivity of iodine monochloride in iodofluorination of fluoroolefins depends significantly on the acidity of the reaction media. For instance, reaction of ICl with tetrafluoroethylene (TFE) in 99% anhydrous hydrogen fluoride in the absence of catalyst produces a mixture of $ClCF_2CF_2I$ (**1**) and C_2F_5I (**2**), isolated in 48% and 19% yields, respectively.[16] The minor component in the

$$ICl + CF_2{=}CF_2 \xrightarrow[\text{HF}]{25\ °C,\ 16\ h} ClCF_2CF_2I + CF_3CF_2I \quad (2)$$
$$(\textbf{1})\ 48\% \qquad (\textbf{2})\ 19\%$$
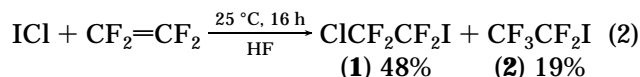
mixture (iodide **2**) is a product of conjugated iodofluorination of TFE, but the major product (iodide **1**) is the result of a well-known thermal reaction of ICl with the olefin.[17]

The presence of Lewis acids drastically changes the course of this reaction, and the yield of desirable pentafluoroethyl iodide (**2**) under the same conditions can be increased to up to 91% by addition of 15−25 mol % of boron trifluoride. In sharp contrast to the data reported in refs 13 and 14, this reaction proceeds rapidly at ambient temperature and produces only trace amounts of the byproduct **1** (Table 1, entries 2, 3).

$$ICl + CF_2{=}CF_2 \xrightarrow[\text{HF/BF}_3]{25\ °C,\ 16\ h}$$
$$ClCF_2CF_2I + \quad CF_3CF_2I \quad (3)$$
$$(\textbf{1})\ 1\% \qquad (\textbf{2})\ 78{-}91\%$$

Only certain Lewis acids capable of significantly increasing the acidity of hydrogen fluoride, such as SbF_5, TaF_5, and NbF_5, effectively catalyze the iodofluorination of TFE. The lower yield of **2** with TaF_5 (Table 1, entry 4) as a catalyst is probably due to low solubility of this compound in HF.[18] On the other hand, catalysts such as $AlCl_3$ and $ZnCl_2$ are not active in this reaction, and no significant difference in the ratio of **1** to **2** over that of the control experiment (without the catalyst) was observed in the reaction of TFE with ICl at 25 °C (Table 1, entries 1, 6, 7).

The reaction of chlorotrifluoroethylene (**3**) and ICl also proceeds under mild conditions and leads to a mixture of two isomeric iodides (**4a,b**) in the ratio 67:33:

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(13) Millauer, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 929.

(14) Millauer, H. Ger. Offen. 2,061,355, 1972; *Chem. Abstr.* **1972**, *77*, 87828n; Ger. Offen. 2,100,140, 1972; *Chem. Abstr.* **1972**, *77*, 125944g.

(15) Deev, L. E.; Nazarenko, T. I.; Pashkevich, K. I.; Ponomarev, V. G. *Uspekhi Khim.* **1992**, *61*, 40, reviews the literature on the synthesis and reactions of perfluoroalkyl iodides.

(16) The reactions discussed in this paper are covered in part by U.S. Patent 5,421,028, 1996, to DuPont; *Chem. Abstr.* **1996**, *123*, P 313381p.

(17) Dyatkin, B. L.; Mochalina, E. P.; Knunyants, I. L. In *Fluorine Chemistry Reviews*; Tarrant, P., Ed.; Marcel Dekker Inc.: New York, 1969; Vol. 3, p 45.

(18) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985; pp 33−64.

Table 1. Reaction of Fluoroolefins with ICl/HF

entry	ICl (mol)	olefin (mol)	HF (mol)	catalyst (mol)	temp (°C)	time (h)	products (yield %)
1	0.3	TFE (0.3)	5	none	25	16	**1** (48) **2** (19)
2	0.3	TFE (0.3)	5	BF₃ (0.074)	50 25	8 10	**1** (1) **2** (78)
3	0.3	TFE (0.3)	5	BF₃ (0.147)	25	18	**1** (1) **2** (91)
4	0.3	TFE (0.3)	5	TaF₅ (0.006)	50 20	8 10	**1** (9) **2** (53)
5	0.3	TFE (0.3)	5	NbF₅ (0.006)	50 20	8 10	**1** (1) **2** (86)
6	0.15	TFE (0.15)	2.5	AlCl₃ (0.011)	50 20	8 10	**1** (36) **2** (11.5)
7	0.3	TFE (0.3)	5	ZnCl₂ (0.011)	25	16	**1** (49) **2** (13)
8	0.3	**3** (0.3)	5	BF₃ (0.147)	25	16	**4a,b** (46)
9	0.3	**5** (0.3)	5	BF₃ (0.147)	25	16	**6** (73)
10	0.3	HFP (0.3)	5	BF₃ (0.147)	50	18	**7** (79)
11	0.3	**8** (0.3)	5	BF₃ (0.147)	50	18	**9** (59)
12	0.3	**10** (0.3)	5	BF₃ (0.147)	50	20	**11** (84)
13	0.3	**12** (0.3)	5	BF₃ (0.147)	70	20	**14** (82)
14	0.3	**13** (0.3)	5	BF₃ (0.147)	90	20	**15** (82)

$$CFCl{=}CF_2 + ICl \xrightarrow[BF_3]{25\ °C,\ 12\ h}$$
(3)

$$CF_3CFClI + ClCF_2CF_2I \quad \text{yield } 46\% \quad (4)$$
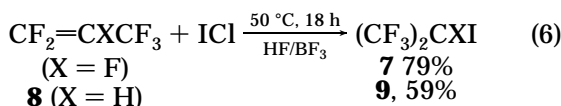$$\textbf{(4a)} \qquad\qquad \textbf{(4b)}$$

This result is in a good agreement with the electrophilic character of the reagent, since electrophilic addition to **3**, in contrast to a radical reaction, is known to be not selective.[3,17]
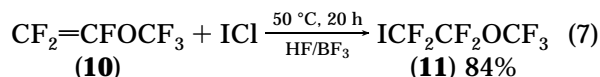
However, the electrophilic addition across the double bond of trifluoroethylene (**5**) is reported to be regiospecific[3,17] and in accordance with the fact that the iodofluorination of **5** proceeds with formation of **6** as the only product

$$CFH{=}CF_2 + ICl \xrightarrow[HF/BF_3]{25\ °C,\ 12\ h} CF_3CFHI \quad (5)$$
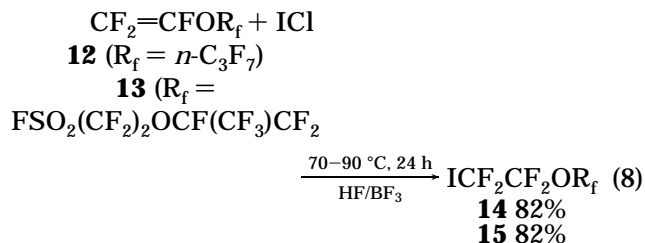$$\textbf{(5)} \qquad\qquad\qquad \textbf{(6)}\ 73\%$$
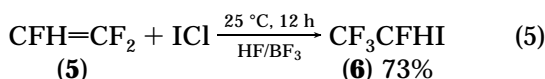
Hexafluoropropylene (HFP) is less reactive than TFE and conjugate addition of "IF" across its double bond proceeds at a reasonable rate only at elevated temperature, producing *i*-C₃F₇I (**7**). Iodide **9** was prepared under similar conditions using 2*H*-pentafluoropropene (**8**) as a starting material.

$$CF_2{=}CXCF_3 + ICl \xrightarrow[HF/BF_3]{50\ °C,\ 18\ h} (CF_3)_2CXI \quad (6)$$
$$(X = F) \qquad\qquad\qquad \textbf{7}\ 79\%$$
$$\textbf{8}\ (X = H) \qquad\qquad\qquad \textbf{9},\ 59\%$$

Perfluorinated vinyl ethers are less active in this reaction than TFE or even HFP, and usually higher temperature and longer reaction time are required to achieve a reasonable conversion of starting material. For instance, perfluoro(methylvinyl) ether **10** reacts with the ICl/HF in the presence of BF₃ producing compound **11**:

$$CF_2{=}CFOCF_3 + ICl \xrightarrow[HF/BF_3]{50\ °C,\ 20\ h} ICF_2CF_2OCF_3 \quad (7)$$
$$\textbf{(10)} \qquad\qquad\qquad\qquad \textbf{(11)}\ 84\%$$

Formation of only one regioisomer in this reaction is in agreement with the report that the reaction of **10** with IF₅/I₂ is regiospecific.[19] Iodofluorination of vinyl ethers **12** and **13** is even slower and is carried out at 70−90 °C. It should be pointed out the combination of ICl/HF/BF₃ is efficient for the iodofluorination of terminal olefins only, since no corresponding iodide was detected in reaction with perfluoropentene-2, even on prolonged (16 h) heating at 200 °C.

$$CF_2{=}CFOR_f + ICl$$
$$\textbf{12}\ (R_f = n\text{-}C_3F_7)$$
$$\textbf{13}\ (R_f =$$
$$FSO_2(CF_2)_2OCF(CF_3)CF_2$$

$$\xrightarrow[HF/BF_3]{70-90\ °C,\ 24\ h} ICF_2CF_2OR_f \quad (8)$$
$$\textbf{14}\ 82\%$$
$$\textbf{15}\ 82\%$$

Mechanistic Considerations. We believe that these electrophilic iodofluorinations of fluoroolefins proceed as a conjugate process and do not involve the formation of iodine monofluoride as an independent intermediate (eqs 9, 10).

$$1)\ HF + I{-}Cl \rightarrow [H{-}Cl{-}I^+]\ (\textbf{16}) \quad (9)$$
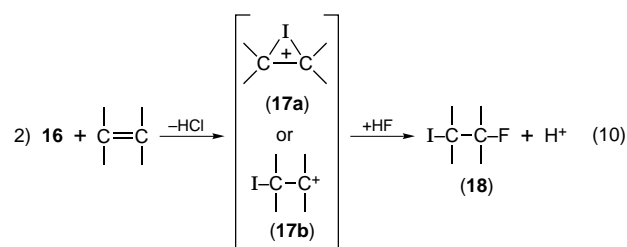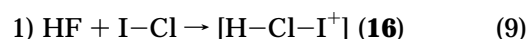
When viewed as a stepwise process, probably the first step of the reaction involves the protonation of iodine monochloride with the generation of highly electrophilic halonium ion agregate **16**, since the ability of halogens such as chlorine, bromine, and iodine to form polynuclear and halonium cations is well known,[20] and the salt H₂Cl⁺SbF₆⁻ was even isolated at low temperature.[21] Electrophilic species **16** is the agent for transfer of I⁺ cation to a double bond with generation of carbocation **17a** or **17b** and a molecule of HCl. Reaction of **17a,b** with the solvent, anhydrous hydrogen fluoride, leads to formation of iodofluorination product **18**. It should be pointed out that the formation of significant amounts of byproduct hydrogen chloride was observed in all reactions.

This mechanism also explains the catalytic effect of *certain* Lewis acids on the iodofluorination process. Anhydrous hydrogen fluoride is a relatively weak protic acid ($-H_0 = 11$ for 99% HF;[18] the value for extremely dry HF is as high as 14.5[22]). However, the acidity of HF can be increased in the presence of a Lewis acid. The addition of compounds such as BF₃, TaF₅, NbF₅, and SbF₅ to HF shifts the $-H_0$ value into the range of 16−20.[18] The acidity of such a superacid mixture correlates directly with the electrophilicity of H⁺ in these solutions so that the yield of iodofluorination product, e.g., **2** from

(19) Lur'e, E. P.; Dyatkin, B. L.; Knunyants, I. L. *Zh. Org. Khim.* **1971**, *7*, 1835.
(20) Reference 18, pp 217−225.
(21) Christie, K. O. *Inorg. Chem.* **1975**, *14*, 2230.
(22) Gillespie, R. J.; Liang, J. *J. Am. Chem. Soc.* **1988**, *110*, 6053.

the reaction of TFE with ICl/HF, is higher when catalyzed by the above-mentioned Lewis acids than in the noncatalyzed process.

Experimental Section

^{19}F and ^{1}H NMR spectra were recorded on a QE-300 (General Electric) instrument using $CFCl_3$ as internal standard and $CDCl_3$ as a lock solvent. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer in the gas phase or in a liquid film. All reagents were commercially available. Compounds **1**, **2**, **4a,b**, **6**, **7**, and **9** were identified by comparison of boiling points with reported values and by ^{19}F NMR, IR, and GC data with those of authentic samples. Iodides **11**[19] and **14**[23] were identified by comparison of ^{19}F NMR, IR, and mass spectral data with literature values.

Caution: Hydrogen fluoride is toxic and causes severe chemical burns. It should be handled by trained personnel only.

General Procedure for the Reaction of ICl with Fluoroolefins in HF. A 400 mL Hastelloy reactor was charged with 0.1–0.3 mol of iodine monochloride, 3–5 mol of HF, 5–25 mol % (based on HF) of the catalyst, and 0.1–0.3 mol of fluoroolefin.

The reactor was kept at 25–90 °C for 12–24 h. Water (100–200 mL) was injected into the reactor at ambient temperature. Iodide **2** (bp 13 °C) was collected in a cold trap (−78 °C) after the gases were slowly bled out of the reactor and fractionated using a low-temperature column. In the case of products **4a,b**, **6**, **7**, **9**, **11**, **14**, and **15**, the reaction mixture was transferred into a polyethylene bottle, and the fluoroorganic (lower) layer was separated, washed twice with water, and dried over P_2O_5. The reaction conditions and isolated yields of products are given in Table 1.

Compound **15** was characterized as follows: bp 130/132 °C/200 mmHg; IR (liquid) 1466 (s), 1322 (m), 1245 (m), 1224 (m), 1205 (m), 1155 (s), 990 (m), 915 (m), 822 (w), 796 (m), 704 (m) cm^{-1}; MS *m/e* 591.8318 (M$^+$, $C_7F_{15}ISO_4^+$, calcd 591.8322); ^{19}F NMR ($ICF_2CF_2OCF_2CF(CF_3)OCF_2CF_2SO_2F$) δ −66.66 (t, 2F), −85.90 (−83.76) (m, 2F), −79.50 (m, 2F), −145.38 (t, 1F), −80.34 (q, 3F), −83.76 (−85.90) (m, 2F, *J* = 6 Hz), 112.38 (m, 2F, *J* = 6 Hz), 45.13 (pent, 1F, *J* = 6 Hz).

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(23) Kokai JP 02,262,529; 90, 262, 529, 1989; *Chem. Abstr.* **1991**, *114*, 142645k.