

Table 1
Isomerization of 1,2-dichlorohexafluoropropane (**1**)^a

No.	ACF (g)	$\text{ClCF}_2\text{CFCICF}_3 \xrightarrow[\text{ACF/promoter}]{130^\circ\text{C}} \text{CF}_3\text{CCl}_2\text{CF}_2$		
		Promoter (mmol)	Time (h)	Conversion of 1 (%) ^{b,c}
1	0.75	None	5 ^d	0.2%
2	0.25	HFP (3)	5	44
3	0.25	None	5	1
4	0.5	HFP (3)	4	67
5	0.5	None	4	0
			23	75
6	0.75	None	5	26
7	0.75	HFP (1.5)	4	98
8	0.75	HFP (6)	4	90
9	0.75	CPFP (1.15)	5	84.1
10	0.5	PFCB (3)	4	76.8
11	0.5	PFCP (3)	4	51.2
12	0.5	PFCH (3)	4	16.8
13	0.5	none	4	11.8
14	1.0	HFP (3)	5	93
15	1.0	None	5	48
16	1.0	CPFP (3)	5	100
17	1.25	HFP (3)	4	100
18	1.25	None	4	47.8
			23	75
19	1.5	HFP (3)	7	100
20	1.5	None	5	87

^a11.1 g (50 mmol) of **1**.

^bBased on IR (gas-phase) and ¹⁹F NMR.

^cSelectivity of all reaction is 100%.

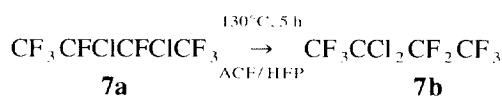
^dReaction run at 50°C.

HFP: hexafluoropropene; CPFP: 2-chloropentafluoropropene; PFCB: perfluorocyclobutene; PFCP: perfluorocyclopentene; PFCH: perfluorocyclohexene.

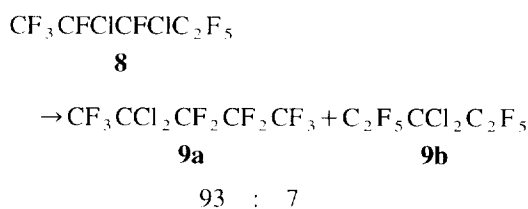
acid (SbF₅) and carbonyl compound [10]. Although 1,2-dichlorotetrafluoroethane (**3**) was claimed [3] to rearrange to 1,1-dichlorotetrafluoroethane (**4**) under mild conditions (reflux with ACF for several hours; the b.p. of **3** is 4°C), it is, actually, surprisingly resistant to the action of ACF. Isomerization does not take place at ambient temperature, and very little if any **4** is seen after prolonged heating at 50°C. The isomerization occurs at higher temperature, but is accompanied by considerable disproportionation. A mixture of **3** and **4** (88:12) with ACF after 15 h at 100°C gives a mixture containing 12% C₂F₅Cl (**5**), 48.4% **4**, 37% CF₃CCl₃ (**6**) and 2.8% **3**. The conversion of starting material at this point is 85%, but the yield of **4** is only 38%. Hexafluoropropene also has a pronounced effect on this process. Compared with the above results, 10 mol% HFP somewhat slows the isomerization of **3** (66% conversion of mixture after 15 h at 100°C) but markedly increases the selectivity and the yield of **4** was 84% based on converted **3** (Table 2).

Higher vicinal dichloroperfluoroalkanes are more reactive towards ACF than propane **1**. The isomerization of dichloride **7a** into **7b** in the presence of the ACF/HFP catalytic system proceeds rapidly at 130°C (96% conversion of **7a** after 5 h

with 100% selectivity, starting with a 56:44 mixture of **7a,b**) (Table 2).



Similarly, isomerization of *F*-2,3-dichloropentane (**8**) containing 4% of *F*-pentene-2 at 130°C in the presence of ACF produced the two isomeric pentanes **9a,b** (93:7 ratio) in 100% yield. Compound **9a** is favored as a thermodynamic product in this process, since a 95:5 ratio of **9a,b** was obtained after the reaction of an 85:15 mixture of **9a,b** with ACF under similar conditions. Note that the reaction proceeded with ACF catalyst only, although over an extended time. We speculate that, in this case, the *F*-pentene-2 impurity (Table 2) may have functioned as a co-catalyst.



The isomerization of vicinal dichloro-*F*-alkanes by the ACF in the presence of fluoroolefin promoter can be explained by either of two candidate mechanisms (both exemplified by the isomerization of **1** to **2**).

The first (Scheme 1) involves an initial reaction between Lewis acid (ACF) and hexafluoropropene to form perfluoroallyl cation, which can then abstract fluorine from either a -CFCl- or CF₂Cl group of **1**, generating carbocations **10a** or **10c**, respectively. Both carbocations are probably in equilibrium with **1**, HFP, and perfluoroallyl cation, but **10a** can rearrange to the more stable cation **10d** by a conventional intramolecular 1,2-migration of Cl via intermediate chloronium cation **10b**. Cation **10d** then irreversibly captures F⁻ from its counter anion to produce the *gem*-dichloro isomer **2**. The likelihood that **10b** forms directly from **1**, bypassing **10a** entirely, is supported by the observations below, suggesting that cycloalkane rearrangements proceed through bridged chloronium or bromonium cations as low energy intermediates. The effective *F*-alkene promoters are therefore limited to those that more readily give perfluoroallyl cations.

The second possible mechanism is an *intermolecular* process for Cl rearrangement catalyzed by HFP (Scheme 2). It involves direct abstraction of F⁻ from either a CFCl- or -CF₂Cl group of **1** by ACF to generate **10c** or **10a**. Rather than rearranging via **10b**, cation **10a** instead transfers Cl⁺ to HFP to give **10f** and CF₃CCl=CF₂ (pathway 'A'), which then returns Cl⁺ regioselectively to CF₃CCl=CF₂ to produce **10d** and regenerate the HFP catalyst (the same process with **10c** just regenerates **1**, pathway 'B'). The HFP promoter thus plays the key role of a 'Cl⁺ shuttle', and the effective *F*-alkene promoters are therefore limited to those that can undergo electrophilic (Cl⁺) addition.

Table 2
Isomerization of halo fluorocarbons

No.	Compound (mmol)	Catalyst ^a	Method	Temperature (°C)	Time (h)	Conversion (%)	Products (wt.%) ^b
1	3, 4' (30)	ACF (1), HFP (3)	B	100	15	3 (66)	3 (23), 4 (75), 5 (1.9)
2	3, 4' (30)	ACF	B	100	15	3 (85)	3 (2.8), 4 (48.4), 4 (48.4), 5 (12), 6 (37)
3	7a,b' (24)	ACF (1), HFP (3)	B	130	5	100	7b (100)
4	8' (25)	ACF (1)	B	130	15	100	9a (93), 9b (7)
5	11a,b' (26)	ACF (1), HFP (3)	B	130	45	11a (16), 11b (62)	11a (47.5), 11b (16.5), 12 (36.5)
6	13a,b' (25)	ACF (1), HFP (3)	B	130	2	13a (36.5), 13b (100)	13a (47), 14 (53)
7	17 (50)	ACF (1)	A	Exothermal	1	100	18 100
8	19 (10)	ACF (0.5)	A	25	5	100	20a (75), 20b (25)
9	20a,b' (10)	ACF (0.5)	A	80	14	–	20a (95), 20b (5)
10	21a,b' (10)	ACF (0.7)	A	25	20	21a (<1), 21b (100)	21a (85), 22 (15)
11	23 (30)	ACF (0.5), HFP (1)	B	130	8	13	23 (87), 24 (13)
12	25 (30), HFP (30)	ACF (1)	B	130	20	25 (33), HFP (95)	HFP (2), 25 (18), 26 (27), 27 (53)
13	29 (50)	ACF (1), HFP (3)	B	80	36	100	30 (100) ^c

^aACF in grams, promoter in mmol.^bBased on ¹⁹F NMR data.^cRatio 88:12.^dRatio 56:44.^eContained 4% *F*-pentene-2.^fRatio 53.5:46.5.^gRatio 74:26.^hRatio 75:25.ⁱRatio 84:16.^jSelectivity 100%.

4. Experimental

^{19}F and ^1H NMR spectra were recorded on QE-300 (General Electric) instrument using CFCl_3 as internal standard and CDCl_3 as a lock solvent. IR spectra were recorded on Perkin-Elmer 1600 FT spectrometer in the gas phase or in a liquid film. Compounds **1**, **7a,b**, **11a,b**, **23**, **25**, **27**, **29** were commercially available (PCR). Alkanes **8**, **13a,b**, **19**, **21a,b** were prepared by photochemical chlorination or bromination of corresponding fluoroolefins. Compounds **2** [12,13], **9a,b** [14], **12**, **15**, **16**, **18** [15], **20a,b** [14], **24** [16], **26** [17], **27**, **30** were identified by comparison of b.p. with reported values and/or by ^{19}F NMR, IR and GC data with those of authentic samples. The aluminum chlorofluoride was prepared by the reaction of CFCl_3 with AlCl_3 [5], and was stored and handled in a dry box. Proper handling of the catalyst is critical, since it is extremely sensitive to atmospheric moisture.

5. Isomerization of haloalkanes (General procedure)

Method A: Inside a dry box, the catalyst was placed in a round-bottomed flask equipped with magnetic stirrer, and the substrate was added slowly over 1 to 5 min to the catalyst under slow flow of nitrogen. The closed reaction mixture was stirred at ambient temperature for 2 to 90 h. The reaction mixture was usually quenched and washed with water, dried over P_2O_5 and analyzed. Reaction conditions and ratio of reactants are given in Tables 1 and 2.

Method B: Inside a dry box, a 75-ml stainless steel cylinder was charged with catalyst followed by the liquid substrates. Gaseous reagents were measured in a Pyrex vacuum line and then condensed into the cold, evacuated reactor containing the catalyst. After the specified reaction time, the contents of the cylinder were removed under vacuum and analyzed by GC and ^{19}F NMR. The reaction conditions and ratio of reactants are given in Tables 1 and 2.

The following compounds were characterized by ^{19}F NMR.

9a: $\text{CF}_3^{\text{A}}\text{CCl}_2\text{CF}_2^{\text{C}}\text{CF}_2^{\text{D}}\text{CF}_3^{\text{B}}$ A -74.28 (3F, m), B -81.35 (3F, t), C -110.69 (2F, m), D -121.83 (2F, m) ppm; $J_{\text{A-C}} = 7$, $J_{\text{B-C}} = 11$ Hz;

9b: -76.53 (3F, pent.), -113.01 (2F, hept) ppm; $J = 4$ Hz;

12: -120.42 (4F, m), -127.40 (2F, m)

14: -119.34 (4F, s), -123.84 (4F, s)

20a $\text{CF}_3^{\text{A}}\text{CBr}_2\text{CF}_2^{\text{C}}\text{CF}_2^{\text{D}}\text{CF}_3^{\text{B}}$ A -70.36 (3F, m), B -81.28 (3F, m), C -104.36 (2F, m), D -120.74 (2F, m) ppm; $J_{\text{A-C}} = 10$, $J_{\text{B-C}} = 12$ Hz;

20b: -76.65 (3F, pent.), -106.73 (2F, hept) ppm; $J = 3.2$ Hz;

22: -112.59 (4F, br. s), -120.50 (4F, br.s)

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