





# Isomerization of halopolyfluoroalkanes by the action of aluminum chlorofluoride <sup>1</sup>

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#### Abstract

A combination of aluminum chlorofluoride (ACF)/fluorooletin is an effective catalytic system for isomerization of *vic*-dichloroperfluoroalkanes into *gem*-isomers. For example, the isomerization of 1,2-dichloro-*F*-propane in the presence of catalytic amounts of ACF and hexafluoropropene proceeds at 130°C giving 2,2-dichloro-*F*-propane in high yield. This catalytic system is also effective for converting cyclic 1,2-dichloro-*F*-cycloalkanes into 1,1-dichloro-*F*-cycloalkanes. Dibromo-*F*-alkanes are more reactive and rearrange under the action of ACF alone at 25–100°C. Primary monoiodo- and monobromo-*F*-alkanes in the presence of ACF are converted into secondary isomers in moderate yields. © 1998 Elsevier Science S.A. All rights reserved.

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#### 1. Introduction

Several isomerizations of dibromopolyfluoroalkanes have been reported to be catalyzed by aluminum halides [1–3]. These reactions generally involve the isomerization of *vic*-dibromides into *gem*-dibromides and can proceed in high yield and conversion. Of the alkanes studied, 1,2-dibromotetrafluoroethane rearranges the most readily, as might be expected from a mechanism involving carbocationic intermediates formed by coordination of catalyst to the appropriate fluorine atoms.

Examples of similar transformations for the less reactive dichloropolyfluoroalkanes are rare, but have been reported to proceed with aluminum chlorofluoride (ACF) as a catalyst [4.5]. Our interest in the use of ACF as an especially effective Lewis acid catalyst [6–8] prompted an investigation of such rearrangements.

## 2. Results and discussion

Aluminum chlorofluoride (ACF), generated in situ from AlCl<sub>3</sub> and CHClF<sub>2</sub>, is reportedly [4] an effective catalyst for the isomerization of 1,2-dichlorohexafluoropropane (1) into 2,2-dichlorohexafluoropropane (2).

$$CF_3CFCICF_2CI \xrightarrow{50^{\circ}C} (CF_3)_2CCI_2$$
1
2

However, all our attempts to reproduce the reaction as described above have failed. The conversion of 1 in the reaction with ACF (4.5 wt.%) at 50°C after 5 h did not exceed 0.2%. Although at higher temperature the conversion is higher, this process is slow and has a tendency to stop after 5 or 6 h, even in the presence of significant amounts of the catalyst (up to 15 wt.%) (Table 1, entries 5, 6, 13, 15, 18, 20).

We have demonstrated that the addition of certain promoters to a mixture of the catalyst and 1 has a dramatic effect on the isomerization. For example, the conversion of 1 (50 mmol) into 2 in the presence of 17 wt.% of ACF and 1.5 mmol of hexafluoropropene (HFP) promoter is 98% after 4 h at 130°C compared to 26% after 5 h in a control experiment without HFP (Table 1, entries 6, 7). Fluoroolefins such as HFP, 2-chloropentafluoropropene, F-cyclobutene and Fcyclopentene were active in this reaction (Table 1) [9]. On the other hand, F-pentene-2, F-2-methylpentene-2, F-4methylpentene-2, 1,1,1-trifluorotrichloropropene, F-allylbenzene, 2.3-dichlorohexafluorobutene-2 and F-cyclohexene were inactive. A possibly related phenomenon is the acceleration of electrophilic cyclization reactions of fluorinated ketones and  $\alpha$ -diketones by addition of F-isobutene or Ftoluene promoter to the reaction mixture containing Lewis

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Table 1 Isomerization of 1,2-dichlorohexafluoropropane (1)<sup>a</sup>

		CICF <sub>2</sub> CFCICF <sub>3</sub>	130 C → CF <sub>3</sub> CO /promoter	Cl <sub>2</sub> CF <sub>+</sub> 2
No.	ACF (g)	Promoter (mmol)	Time (h)	Conversion of 1 (%) <sup>b.c</sup>
1	0.75	None	5 <sup>d</sup>	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	9()
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

<sup>&</sup>lt;sup>a</sup>11.1 g (50 mmol) of 1.

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

acid (SbF<sub>5</sub>) and carbonyl compound [10]. Although 1,2dichlorotetrafluoroethane (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  $12\% \text{ C}_3\text{F}_5\text{Cl}(5)$ , 48.4% 4,  $37\% \text{ CF}_3\text{CCl}_3(6)$  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).

$$CF_3 CFCICFCICF_3 \xrightarrow{130^{\circ}C, 5 \text{ h}} CF_3 CCl_2 CF_2 CF_3$$

$$7a \qquad 7b$$

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.

$$CF_3CFCICFCIC_2F_5$$

$$\mathbf{8}$$

$$\rightarrow CF_3CCl_2CF_2CF_2CF_3 + C_2F_5CCl_2C_2F_5$$

$$\mathbf{9a} \qquad \mathbf{9b}$$

$$\mathbf{93} : 7$$

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 CF<sub>2</sub>Cl 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 perfluoroally 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 - CF<sub>2</sub>Cl group of 1 by ACF to generate 10c or 10a. Rather than rearranging via 10b, cation 10a instead transfers Cl<sup>+</sup> to HFP to give 10f and CF<sub>3</sub>CCl=CF<sub>2</sub> (pathway 'A'), which then returns Cl<sup>+</sup> regioselectively to CF<sub>3</sub>CCl=CF<sub>2</sub> 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<sup>+</sup> shuttle', and the effective F-alkene promoters are therefore limited to those that can undergo electrophilic (Cl<sup>+</sup>) addition.

<sup>&</sup>lt;sup>b</sup>Based on IR (gas-phase) and <sup>19</sup>F NMR.

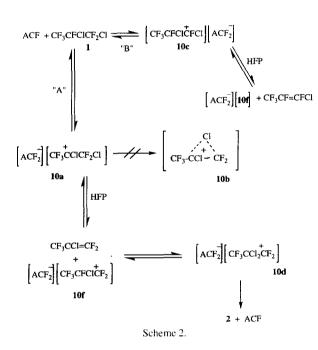
Selectivity of all reaction is 100%.

dReaction run at 50°C.

Isomerization of halofluorocarbons

0.	Compound (mmol)	Catalyst <sup>a</sup>	Method	Temperature (°C) Time (h) Conversion (%)	Time (h)	Conversion (%)	Products (wt.%) <sup>h</sup>
	3, 4° (30)	ACF (1), HFP (3)	В	100	15	3 (66)	3 (23), 4 (75), 5 (1.9)
	3, 4° (30)	ACF	В	100	15	3 (85)	3 (2.8), 4 (48.4), 4 (48.4), 5 (12), 6 (37)
	<b>7a,b</b> <sup>d</sup> (24)	ACF (1), HFP (3)	В	130	5	100	7b (100)
	<b>8</b> ° (25)	ACF (1)	В	130	15	001	9a (93), 9b (7)
	11a,b' (26)	ACF (1), HFP (3)	В	130	45	11a (16), 11b (62)	11a (47.5), 11b (16.5), 12 (36.5)
	<b>13a,b</b> <sup>₽</sup> (25)	ACF (1), HFP (3)	В	130	2	13a (36.5), 13b (100)	13a (47), 14 (53)
	17 (50)	ACF (1)	A	Exothermal		100	<b>18</b> 100
	<b>19</b> (10)	ACF (0.5)	V	25	5	100	20a (75), 20b (25)
	<b>20a,b</b> <sup>h</sup> (10)	ACF (0.5)	Α.	08	41	1	<b>20a</b> (95), <b>20b</b> (5)
	<b>21a,b</b> <sup>†</sup> (10)	ACF (0.7)	Ą	25	20	<b>21a</b> (<1), <b>21b</b> (100)	<b>21a</b> (85), <b>22</b> (15)
	23 (30)	ACF (0.5), HFP (1)	В	130	∞	13	<b>23</b> (87), <b>24</b> (13)
	25 (30), HFP (30)	ACF (1)	В	130	20	25 (33), HFP (95)	HFP (2), 25 (18), 26 (27), 27 (53)
	29 (50)	ACF (1), HFP (3)	В	80	36	100	30 (100)

"ACF in grams, promoter in mmol."
"Based on 19F NMR data.
"Ratio 88:12.
"Ratio 56:44.
"Contained 4% F-pentene-2.
"Ratio 53:5:46.5.
"Ratio 74:26.
"Ratio 75:25.
"Ratio 84:16.
"Selectivity 100%.



Although arguments can be made to favor one mechanism over the other (see below), there are no definitive experimental data to rule out either possibility.<sup>2</sup>

F-1,2-Dichlorocyclobutane (a 53.5:46.5 mixture of trans-11a and cis-11b) is less reactive than the open-chain analog 7a. The isomerization by the ACF/HFP catalytic system is slow at 130°C, and even after 45 h the conversion of 11a,b into 1,1-dichlorohexafluorocyclobutane 12 did not exceed 37%. However, this reaction is surprisingly selective towards the cis-isomer 11b wherein it undergoes a 69% conversion to 12 (100% selectivity) in contrast to a 16% conversion for 11a.

11a (trans): 11b (cis) 12 : 11a : 11b

56.5:43.5 36.0 : 47.5 : 16.5

*Trans*-(**13a**) and *cis*-(**13b**) 1,2-dichloro-*F*-cyclopentane (ratio 74:26) isomerize faster than **11a,b** and do not require a promoter. The rate of isomerization of *cis*-isomer is once again higher than that of *trans*-isomer (92% conversion of **13b** vs. 42% for **13a** after 24 h at 130°C).

Cl 
$$\frac{130^{\circ}\text{C, 2h}}{\text{ACF}}$$
 F  $\frac{\text{Cl}_2}{\text{14}}$  +  $13\text{a}$  +  $13\text{b}$   
13a (trans) 13b (cis) 14 13a 13b  
74 : 26 55 : 43 : 2

An apparently multistep transformation of a 1,3- to 2,2-dichloropropane was observed earlier [5] in the reaction of 1,3-dichloro-1-hydro-*F*-propane (**15**) with ACF.

CICFHCF<sub>2</sub>CF<sub>2</sub>CI 
$$\xrightarrow{ACF}$$
 CHF<sub>2</sub>CCI<sub>2</sub>CF<sub>3</sub>
15 16

Dibromoperfluoroalkanes are more reactive than the dichlorides toward aluminum chlorofluoride. Thus, the isomerization of F-1,2-dibromopropane (17) to gem-dibromopropane 18 in the presence of ACF only is exothermic. In contrast, catalysis of this reaction by AlBr<sub>3</sub>, which is considered to be a strong Lewis acid, requires more drastic conditions (150°C, 3 d) [1].

$$CF_3CFBrCF_2Br \rightarrow (CF_3)_2CBr_2$$
**17 18** (100%)

Isomerization of 2,3-dibromo-*F*-pentane (19) proceeds at ambient temperature to produce a 75:25 mixture of 20a,b. Once again, as in the case of dichloropentanes 10a,b, the *gem*-dibromo isomer 20a is favored, and at higher temperature, the ratio of isomers is increased to 95:5.

CF<sub>3</sub>CFBrCFBrCF<sub>2</sub>CF<sub>3</sub>
19
$$\xrightarrow{25^{\circ}C,5^{\circ}b} CF_3CBr_2C_3F_7 + (C_2F_5)_2CBr_2$$
20a 20b

The reaction of 1,2-dibromo-*F*-cyclopentane **21a,b** with ACF to give **22** also proceeds at 25°C and with high selectivity towards *cis*-isomer. One hundred percent conversion of *cis*-isomer **21b** was achieved after 20 h at ambient temperature in contrast to less than 1% conversion for *trans*-isomer **21a**.

<sup>&</sup>lt;sup>2</sup> The role of bridged chloronium ions is obviously the key distinguishing feature of the two mechanisms. Although the favorability of hydrocarbon halonium ion formation is well known to increase in the order Cl < Br < I (G.A. Olah, Halonium Ions, Wiley, New York, 1975), there are no experimental data on polyfluorinated halonium ions. Theoretical calculations of the relative energies of **10a** vs. **10b** and their bromonium analogs are in progress (D.A. Dixon).

16

15

Scheme 3 provides an explanation for the higher rate of isomerization of *cis*-isomers in polyfluorocycloalkanes and is based on the well-known effect of anchimeric assistance.

85

The reaction starts with electrophilic attack by ACF on fluorine in one of the -CFCl- groups. The synchronous process involves development of an empty orbital on the opposite side of the ring system. A chlorine atom, located in the cisisomer on the same side of the ring interacts with the empty orbital as it forms, minimizing the energy barrier as depicted by A. 1,2-Shift of Cl proceeds through the presumed intermediate (chloronium cation **B**) and finally leads to the formation of gem-dichlorocycloalkane. The formation of a stabilized carbonium ion is responsible for the higher rate of isomerization with cis-isomers, since a similar process for trans-isomers requires not partial, but full ionization of a C-F bond with consequent generation of charge-localized carbocation. Higher reactivity of bromocyclopentane 21b compared to chlorocyclopentane 13b is in good agreement with the proposed mechanism, since it is well established that the ability of halogens to stabilize a positive charge in a  $\beta$ -position increases in the order (F < Cl < Br < 1). Although ethylenehalonium cations containing I, Br and Cl have been generated in solution and thoroughly characterized by NMR spectroscopy<sup>2</sup>, no evidence for the formation of corresponding fluoronium cations has been reported so far. Indeed, calculations indicate that bridged fluoronium ions should exist only as highly energetic transition states [6].

These results can also be explained by the alternative mechanism proposed above (Scheme 2) for the 1,2-dichloro-*F*-cycloalkane rearrangements. The observed greater reactivity of the *cis*- vs. *trans*-isomers might simply reflect the more favorable approach of ACF to a C–F bond in the *cis*-isomer, which does not involve steric interaction with an adjacent C–Cl bond. The facile rearrangements of both acyclic and cyclic 1,2-dibromo-*F*-alkanes by ACF in the absence of any promoter, however, suggests a mechanism involving bridged bromonium ion intermediates in both cases.

The reactivity of monobromoperfluoroalkanes toward isomerization is very low. Elevated temperatures and a promoter are required. Despite high selectivity, the conversion

$$(CF_{2})_{\widehat{n}}$$

$$X$$

$$X$$

$$F$$

$$ACF$$

of a starting material does not exceed 15–30%, probably due to deactivation of the catalyst. For example, the reaction of 1-bromo-*F*-propane (**23**) with the ACF/HFP catalytic system produces 2-bromo-*F*-propane (**24**) in only 13% conversion (100% selectivity).

$$CF_3CF_2CF_2Br \xrightarrow{130^{\circ}C.16 \text{ h}} (CF_3)_2CFBr$$
23 (CF<sub>3</sub>)<sub>2</sub> CFBr
24, 100% yield (13% conversion)

The reaction of 1-bromo-*F*-butane (**25**) with an equimolar amount of HFP in the presence of ACF under similar conditions results in a 55:28:17 mixture of **25**, 2-bromo-*F*-butane (**26**) and alkene **27**.

$$CF_{3}CF_{2}CF_{2}Br + CF_{2} = CFCF_{3}$$
25
$$CF_{3}CF_{2}CF_{3}Br + CF_{3}CFF_{3}$$

$$CF_{3}CFBrCF_{2}CF_{3} + (CF_{3})_{2}C = CFC_{2}F_{5} + 25$$
26
27

**26**, 95% yield (33% conversion)

The formation of olefin **27** in this reaction is a result of the well-known electrophilic dimerization of HFP [7,11], which obviously competes with the isomerization. On the other hand, the absence of i- $C_3F_7Br$  in the reaction mixture is evidence that the isomerization of **25** proceeds via an intramolecular 1,2-shift of bromine in intermediate carbocation **28** and does not involve a transfer of  $Br^+$  to a molecule of HFP.

$$\begin{bmatrix} Br \\ CF_2 - CF C_2F_5 \end{bmatrix}$$
28

F-propyl iodide (29) is much more active in the isomerization reaction than bromide 23. The reaction in the presence of ACF/HFP catalyst proceeds already at 80°C to give secondary iodide 30 in quantitative yield.

$$CF_3CF_2CF_2I \xrightarrow{80^{\circ}C, 36 \text{ h}} (CF_3)_2CFI$$
29  $ACF/HEP$  30

### 3. Conclusions

ACF is an excellent catalyst for isomerization of *vic*-dibromoperfluoroalkanes and -cycloalkanes to *gem*-dibromides in high yield and conversions under mild conditions. The more recalcitrant *vic*-dichlorides require a combination of ACF and a promoter fluoroolefin, such as hexafluoropropene, for clean and rapid conversion to the corresponding *gem*-dichlorides. The catalyst system ACF/HFP even allows for the efficient rearrangement of primary bromides and iodides to their secondary isomers.

## 4. Experimental

<sup>19</sup>F and <sup>1</sup>H NMR spectra were recorded on QE-300 (General Electric) instrument using CFCl<sub>3</sub> as internal standard and CDCl<sub>3</sub> 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 <sup>19</sup>F NMR, IR and GC data with those of authentic samples. The aluminum chlorofluoride was prepared by the reaction of CFCl<sub>3</sub> with AlCl<sub>3</sub> [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 <sup>19</sup>F NMR. The reaction conditions and ratio of reactants are given in Tables 1 and 2.

The following compounds were characterized by <sup>19</sup>F NMR.

**9a**:  $CF_3^ACCl_2CF_2^CCF_2^DCF_3^B$  A -74.28 (3F m), B -81.35 (3F, t), C -110.69 (2F, m), D -121.83 (2F, m) ppm;  $J_{A-C} = 7$ ,  $J_{B-C} = 11$  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** CF<sub>3</sub><sup>A</sup>CBr<sub>2</sub>CF<sub>2</sub><sup>C</sup>CF<sub>2</sub><sup>D</sup>CF<sub>3</sub><sup>B</sup> A -70.36 (3F m), B -81.28 (3F, m), C -104.36 (2F, m), D -120.74 (2F, m) ppm;  $J_{A-C} = 10$ ,  $J_{B-C} = 12$  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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