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Electrophilic reactions of fluorocarbons under the action of aluminum chlorofluoride, a potent Lewis acid [1]

V.A. Petrov *, C.G. Krespan, B.E. Smart

DuPont Central Research and Development, Experimental Station, P.O. Box 80328, Wilmington, DE 19880-0328, USA

Abstract

A new Lewis acid – aluminum chlorofluoride – was demonstrated to be an effective catalyst for the isomerization of fluoroolefins, polyfluorinated epoxides and cyclopropanes. At ambient temperature this catalyst converts perfluorobutadiene-1,3 into perfluorobutyne-2 and perfluoro(4-methylpentene-2) into perfluoro(2-methylpentene-2) in nearly quantitative yield. At 100 °C, aluminum chlorofluoride causes the cleavage of perfluorinated tertiary amines.

Keywords: Electrophilic reactions; Fluorocarbons; Aluminum chlorofluoride; Lewis acid; NMR spectroscopy

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1. Introduction

The Lewis acid aluminum chlorofluoride (ACF), in marked contrast to the moderately active $AlCl_3$ and the nearly inert AlF_3, is an extremely effective catalyst for the isomerization of CF_2ClCCl_2F [1], the condensation of halomethanes [2] and some fluoroolefins [3,4] with fluoroethylenes, and for the [2+2] electrophilic cycloaddition of hexafluoroacetone to fluoroethylenes [5]. It is readily generated by reacting $AlCl_3$ with organofluorine compounds such as CF_2ClCCl_2F [1], $CFCl_3$, $CHCl_2F$ or $CF_3CF{=}CF_2$ [2,3]. As a moisture-sensitive but easily handled solid that does not fluorinate olefinic double bonds or cause replacement of halogen atoms by fluorine, ACF is in many ways superior to SbF_5, which is one of the strongest Lewis acids widely used in the synthesis of fluorocarbons [6,7]. For example, if effectively catalyzes the condensations of tetrafluoroethylene with perfluoropentene-2 and perfluorocyclopentene [23], which fail when SbF_5 is used [7].

This paper describes the use of ACF to promote three different types reactions of fluorocarbons: (a) isomerization of olefins, epoxides and cyclopropanes; (b) cleavage of tertiary perfluorinated amines; and (c) dimerization of hexafluoropropene.

2. Results and discussion

ACF, like antimony pentafluoride [7], isomerizes terminal fluoroolefins. Iodine-free perfluroallyl iodide (1) reacts exothermically with a catalytic amount of ACF to form a 1:1 mixture of *trans* and *cis* isomers of perfluoro-1-iodopropene (2) in 90% yield.

$$\underset{(\mathbf{1})}{ICF_2CF=CF_2} \xrightarrow[ACF]{\text{exothermic}} \underset{(\mathbf{2})\ (90\%)}{ICF=CFCF_3}$$

Similarly, perfluoroallylbenzene (3) and ACF quantitatively give a mixture of *cis*- and *trans*-perfluoro-1-phenylpropene-1 (4).

$$\underset{(\mathbf{3})}{C_6F_5CF_2CF=CF_2} \xrightarrow[ACF]{25\ ^\circ C,\ 2\ h} \underset{\substack{(\mathbf{4})\ (100\%)\\ cis/trans = 46:54}}{C_6F_5CF=CFCF_3}$$

Antimony pentafluoride isomerizes perfluoro-1-alkenes selectively to perfluoro-2-alkenes under rather mild conditions [8], but further migration of the double bond can be achieved only by prolonged heating of the olefin with SbF_5 [7,9]. ACF is more active than SbF_5 in the isomerization of long-chain fluoroolefins. For example, the isomerization of perfluoroheptene-1 (5) with catalytic ACF proceeds at room temperature (see Table 1). After 1 h, no starting material remained and a 65:35 mixture of perfluoroheptene-2 (7)/perfluoroheptene-3 (6) was produced.

$$\underset{(\mathbf{5})}{CF_2=CFCF_2CF_2C_3F_7} \xrightarrow[ACF]{25\ ^\circ C,\ 2\ h}$$

$$\underset{(\mathbf{7})}{CF_3CF=CFCF_2C_3F_7} + \underset{(\mathbf{6})}{CF_3CF_2CF=CFC_3F_7}$$

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* Corresponding author.

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Table 1
Isomerization of perfluoroheptene-1 with ACF

Time (h)	Olefin-2 [a]		Olefin-3 [a]	
	trans Isomer	*cis* Isomer	*trans* Isomer	*cis* Isomer
1	59.3	6.4	32.0	2.3
18	15.1	1.4	78.5	4.9
66	5.2	0.9	88.8	5.2
90	5.0	0.8	89.2	5.0

[a] Weight percentages ascertained by ^{19}F NMR spectroscopy.

Isomers **7** and **6** equilibrate more slowly and the isomerization appears to be complete in about 70 h at 25 °C with 94% of **6** in the equilibrium mixture. By contrast, the **7**/**6** ratio reported for the isomerization **5** by SbF_5 as a homogeneous catalyst at 60–70 °C is quite different. Here a mixture of 20%–25% of **6** and 75%–80% of **7** was produced [7].

Unlike typical SbF_5-catalyzed reactions, the isomerizations promoted by ACF are heterogeneous. Notably, a sample of the above reaction mixture filtered after 1 h did not change composition with time. This implies that ACF is completely insoluble and that the reaction is operating through adsorption/desorption at active sites on the surface of the catalyst.

ACF readily isomerizes perfluoro(4-methylpentene-2) (**8**) to perfluoro(2-methylpentene-2) (**9**), isolated in 94% yield.

$$\underset{(\mathbf{8})}{(CF_3)_2CFCF=CFCF_3} \xrightarrow[\text{ACF}]{25\ ^\circ\text{C, 24 h}} \underset{(\mathbf{9})}{(CF_3)_2C=CFC_2F_5}$$

In marked contrast, there is no evidence for this isomerization in the presence of SbF_5 at temperatures up to 70 °C, since electrophilic dimerization of hexafluoropropene with SbF_5 at this temperature forms compound **8** to the exclusion of **9** [10].

ACF and perfluorobutadiene **10** produce perfluorobutyne-2 (**11**) in nearly quantitative yield.

$$\underset{(\mathbf{10})}{CF_2=CFCF=CF_2} \xrightarrow[\text{ACF}]{25\ ^\circ\text{C, 2 h}} \underset{(\mathbf{11})\ (98\%)}{CF_3C\equiv CCF_3}$$

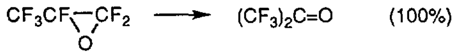
This reaction provides a synthetically useful route to **11** since it proceeds rapidly at room temperature, does not produce any by-products and is easy to scale-up. Antimony pentafluoride, however, cannot be used since polyfluorinated 1,3-dienes give organoantimony compounds via the addition of SbF_5 to a double bond of the corresponding allene intermediate in the diene-acetylene isomerization [11].

Hexafluoropropene oxide (**12**) reacts rapidly with ACF at room temperature to form hexafluoroacetone (**13**), a well-known reaction for SbF_5 [12]. The advantage with ACF is that no purification is required since the catalyst is a non-volatile solid completely insoluble in the product.

Table 2
Reaction of fluorocarbons catalyzed by ACF

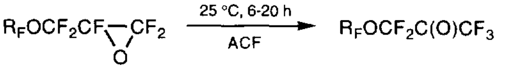
Exp. No.	Compound (mmol)	ACF (g)	Method	Temp. (°C)	Time (h)	Products (yield %)
1	**1** (8)	0.2	A	0–35 [a]	1	**2** (90) [b]
2	**3** (10)	0.2	A	20–35 [a]	2	**4** (100) [c,d]
3	**5** (14)	0.2	A	25	90	**6**, **7** (100) [c,e]
4	**8** (100)	2	B	80	24	**9** (94)
5	**10** (10)	0.3	B	25	2	**11** (100) [c]
6	**12** (20)	0.5	B	25	1	**13** (95)
7	**14** (3)	0.2	A	25	6	**16** (100) [c]
8	**15** (3)	0.2	A	25	20	**17** (100) [c]
9	**18** (19)	0.5	B	150	20	**19a,b** (95) [c,f]
10	**20** (51)	3	B	100	10	**21** (98)
11	**22 (50)**	0.5	B	25	3	**23** (96) [g]
12	**24** (50)	1	B	100	3	**25a,b** (95) [c,h]
13	**26** (10)	3	B	100	4	**27**, **8**, **28** (93) [i]
14	**27** (50)	1	B	25	20	**8**, **9** (95) [j]
15	**27** (50)	1	B	80	20	**9** (85)
16	**29** (51)	3	B	150	20	**30** (78)
17	**31** (100)	3	B	100	20	**32** (68)

[a] Exothermic reaction.
[b] Mixture of *trans* and *cis* isomers (75:25).
[c] Yield based on NMR data.
[d] Mixture of *trans* and *cis* isomers (54:46).
[e] See Table 1.
[f] Ratio 1:1 (GC, ^{19}F NMR), 75% conversion of **18**.
[g] Mixture of *trans* and *cis* isomers (75:25).
[h] Ratio 1:1 (NMR), 60% conversion of **24**.
[i] Ratio 63:33:4 (NMR).
[j] Ratio 30:70 (NMR).



(12) (13)

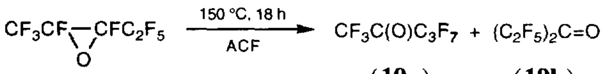
ACF also isomerizes epoxides **14** and **15** to **16** and **17**, respectively, in high yields, although the reaction is slower than with HFPO.



(**14**) $R_F = C_6F_5$- (**16**) (100%)

(**15**) $R_F = CNCF_2CF_2$- (**17**) 100%)

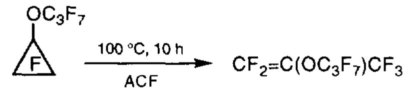
The much less reactive epoxide **18** isomerizes at a noticeable rate only at 150 °C to give the expected [13] mixture of perfluoropentanone-2 (**19a**) and perfluoropentanone-3 (**19b**) in a 1:1 ratio.



(**18**) (**19a**) (**19b**)

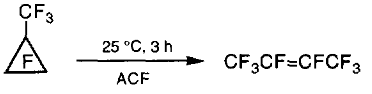
(75% conversion, 95% yield)

ACF effects the isomerization of fluorinated cyclopropanes. Perfluoropropoxycyclopropane (**20**) is converted to the corresponding vinyl ether **21** in very high yield by heating with a catalytic amount of ACF.



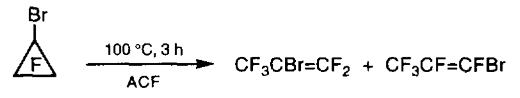
(**20**) (**21**) (98%)

Like the reaction catalyzed by SbF_5 [14], cyclopropane **22** is readily converted into perfluorobutene-2 (**23**) by the action of ACF at ambient temperature.



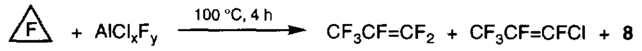
(**22**) (**23**) (96%)

ACF also promotes the isomerization of halocyclopropanes, but not selectively. Bromopentafluorocyclopropane (**24**), for example, reacts with ACF to give a 1:1 mixture of **25a/25b**.



(**24**) (**25a**) (**25b**) (95%)

Perfluorocyclopropane (**26**) itself is converted to hexafluoropropene (**27**) accompanied by dimer **8** and olefin **28** in the reaction with excess ACF.



(**26**) (**27**) (**28**)

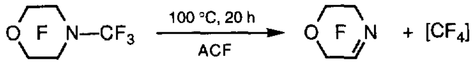
The product **28** obviously arises from an exchange reaction between hexafluoropropene (HFP) and the ACF catalyst, and **8** undoubtedly comes from the electrophilic dimerization of the HFP, which is known to be catalyzed by SbF_5 [9]. Unexpectedly, however, only the kinetic dimer **8** and none of its thermodynamic isomer **9** was observed. Our control experiments show that ACF dimerizes HFP to a 30:70 mixture of **8**/**9** at room temperature, and at 80 °C *only* **9** is formed (85% isolated yield). The reason for the exclusive formation of the byproduct **8** when **9** would be expected under the conditions used for isomerization of **26** is unclear.

ACF cleaves perfluorinated tertiary amines to form an equimolar mixture of imidoyl fluoride and alkane. Thus, heating $(C_4F_9)_3N$ with a catalytic amount of ACF produces perfluorobutane and imine **30**, isolated in 78% yield.

$$(C_4F_9)_3N \xrightarrow[\text{ACF}]{150\ °C,\ 24\ h} C_4F_9N=CFC_3F_7+C_4F_{10}$$

(**29**) (**30**)

Under similar conditions, the morpholine **31** is converted to the cyclic imine **32**.



(**31**) (**32**) (68%)

Although there is no significant difference in activity between ACF and antimony pentafluoride in promoting the cleavage of perfluorinated amines [14–19], ACF seems to be more sensitive to the impurities in the starting material. A significant difference in the reaction rate is observed when technical (85%) versus purified (95%) perfluorotributylamine is used for the reaction with ACF, which was not the case for SbF_5.

3. Experimental details

^{19}F and NMR spectra were recorded on a QE-300 (General Electric) instrument using $CFCl_3$ as internal standard and $CDCl_3$ as lock solvent. IR spectra were recorded on a Perkin–Elmer model 983G spectrometer in the gas phase or as a liquid film.

Compounds **6**, **7**, **8**, **9**, **11**, **23** and hexafluoroacetone were identified by comparison of the ^{19}F NMR and IR data with data obtained for authentic samples.

Compounds **2** [20], **4** [21], **19a,b** [13], **21** [14], **25a** [20], **25b** [21], **28** [22], **30** [15] and **32** [23] were identified by comparison of ^{19}F NMR, IR and mass spectral data with literature values.

3.1. Reagents

Compounds **3**, **5**, **8**, **9**, **10**, **12**, **29** (PCR) and **31** (3M) were obtained from commercial sources and used without further purification. Compound **18** [13] was prepared by oxidation of perfluoropentene with sodium hypobromide using the literature procedure [24]. The aluminum chlorofluoride was prepared by the reaction of $CFCl_3$ with $AlCl_3$ [2], and was stored and handled in a dry box. Proper handling of the catalyst is critical since it is sensitive to atmospheric moisture.

3.2. General procedure

Method A

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

Method B

A 75-ml stainless steel cylinder was charged with the catalyst inside a dry box 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 methods. The reaction conditions and ratio of reactants are given in Table 2.

Compounds **16** and **17** were characterized as follows.

Compound **16**: IR (liq.) (cm^{-1}): 1802. ^{19}F NMR $CF_3^AC(O)CF_2^BOC_6F_5$ δ: −74.87 (t, $3F_A$, $J_{A-B}=12$ Hz); −78.59 (m, $2F_B$); −154.50 (t, 2F, *ortho*); −160.98 (dt, 2F, *meta*); −151.11 (m, 1F, *para*) ppm. Analysis: Calc. for $C_9F_{10}O_2$: C, 32.75; F, 57.56%. Found: C, 33.03; F, 57.36%.

Compound **17**: IR (liq.) (cm^{-1}): 1807. ^{19}F NMR $CF_3^AC(O)CF_2^BOCF_2^CCF_2^DCN$ δ: −74.83 (t, $3F_A$, $J_{A-B}=11$ Hz); −78.10 (m, $2F_{B(C)}$); −86.71 (m, $2F_{C(B)}$); −109.17 (t, $2F_D$) ppm. Analysis: Calc. for $C_6F_9NO_2$: C, 24.93; F, 59.15%. Found: C, 24.94; F, 59.25%.

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