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A NEW GENERAL SYNTHESIS ROUTE TO 1,1,1-TRIHALOPOLYFLUOROALKANES

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SUMMARY

1,1,1-Trichloro- and tribromo polyfluoroalkanes have been synthesized from perfluoroalkyl iodides and anhydrous aluminum chloride and bromide respectively. The reaction is also applicable to perfluoroalkylether iodides, though varying amounts of by-products are formed depending on the structure of the starting iodide.

INTRODUCTION

A number of fluorinated compounds are known to react with Lewis acids, as for example anhydrous aluminum chloride or bromide, leading to substitution of fluorine by chlorine or bromine [1]. Disproportionation as well as isomerization reactions in presence of aluminum halides have also been reported

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[2]. It appears that the reactions of perfluoroalkyl iodides (R_fI) with anhydrous aluminum halides have not received much attention. One example of such an interaction reported is the isomerization of 2-chloro-1,2,2-trifluoroethyl iodide by anhydrous aluminum chloride at 21-23°C to yield a mixture of two products [3]. Similar reactions using methyl iodide as the reaction medium are also reported to yield mixtures of products [4].

Our studies on the reactions of perfluoroalkyl and perfluoroalkylether iodides with anhydrous aluminum chloride and aluminum bromide are reported in this paper.

RESULTS AND DISCUSSION

Initial studies were carried out with n-$C_8F_{17}I$ (I) at atmospheric pressure using 1-3 molar equivalents of anhydrous $AlCl_3$. Heating the reactants together at 60-80°C led to slow sublimation of iodine and formation of $CF_3(CF_2)_6CCl_3$ (II) in low but varying yields depending on the temperature and ratio of the reactants. Under these conditions, substantial amounts of I remained unreacted. For example, a reaction conducted with equimolar amounts of I and $AlCl_3$ at 80°C for 20 h is represented in Scheme 1. In this reaction, about 25 percent of I remained unreacted.

$$\underset{(I)}{CF_3(CF_2)_6CF_2I} \xrightarrow[\text{2) Hydrolysis}]{\text{1) }AlCl_3} \underset{(II)\,(28\%)}{CF_3(CF_2)_6CCl_3} + \underset{(III)\,(15\%)}{CF_3(CF_2)_6CCl_2I}$$

$$+ \underset{(IV)\,(2.7\%)}{CF_3(CF_2)_6COOH}$$

Scheme 1

Since an acid analogous to IV was not detected in any of the other reactions described, it is possible that this reaction at 80°C was carried out in the inadvertent presence of traces of water, to give some R_fCOCl and thence IV by hydrolysis. It is noteworthy that compound III, identified by GC/MS, was not detected in any reaction conducted above 100°C. Its formation at lower temperatures (80°C) would indicate that it is an intermediate from which II is formed. This observation together with the isolation of XII from reaction of X with $AlCl_3$ (Table 1) lead us to believe that the fluorine atoms are made more reactive towards Lewis acids by an iodine or bromine present on the same carbon. Similar activation of the C-F bonds by an adjacent oxygen atom is seen in the initial replacement of α-fluorines by chlorine when fluoroalkylethers are heated with anhydrous $AlCl_3$ [5]. However, the possibility that compounds such as III and XII could be formed from the trichlorocompounds II and XI respectively by reaction with a pure or mixed aluminum halide generated during the reaction, though unlikely, cannot be completely ruled out.

The reaction between I and anhydrous aluminum chloride was also carried out in different solvents. The product II was not formed in any significant amounts when the reaction was carried out in nitromethane at 90°C or in refluxing carbon tetrachloride. In reactions using methylene chloride or $ClCF_2CFCl_2$ as solvents, II was indeed formed along with products formed by the interaction of solvents and aluminum chloride. Reaction of I with three equivalents of $AlCl_3$ in refluxing sulfuryl chloride gave II in 40 percent yield; but the sulfuryl chloride had to be frequently replenished and even then the starting iodide could not be completely transformed.

The best isolated yield (55 percent) was obtained when I was heated with 3.0 equivalents of anhydrous $AlCl_3$ in a stainless-steel pressure vessel at 115-120°C for 24 hrs. This method also made the purification of product II, relatively easy as it was free from the starting iodide, whose presence in the reaction mixture led to liberation of free iodine during distillation. Similarly, $n\text{-}C_{10}F_{21}I$ (V) gave $CF_3(CF_2)_8CCl_3$ (VI) in 55 percent isolated yield. In these reactions, dark intractible materials were always formed, which may result in the reduced yields of the primary products II and VI.

In order to ascertain the general nature of this reaction, the study was extended to a diiodide, a perfluoroalkyl bromide and also perfluoroalkylether iodides. In addition, the reaction of I with anhydrous $AlBr_3$ was also studied. The results are presented in Table 1.

With 1,4-diiodoperfluorobutane (VII), the expected product VIII was contaminated with substantial amounts of perchlorobutadiene (IX). Since the separation of these two components by distillation proved difficult, a sample of VIII was isolated by preparative gas chromatography and was subsequently characterized. Reaction of the bromide, X with $AlCl_3$ required more drastic conditions than those used for iodides, and even at 175-180°C, after 64 h, about 32 percent of the starting bromide was left unreacted.

For the reactions of iodides containing an ether linkage, such as XIII and XV, a lower temperature (100-105°C) was used in order to suppress substitution of fluorine on carbon atoms alpha to the oxygen. It has been reported earlier [6] that acid halides containing perfluoroalkylether functions could be

TABLE 1

Reactions of R_fI and R_fBr with anhydrous AlX_3

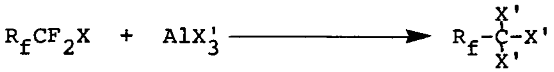
Fluorinated Halides (R_fX)	Aluminum Halide (AlX_3)	Molar Ratio (R_fI: AlX_3)	Temp (°C) Time (Hrs)	Product(s)[1]	Yield (%)[2]
n-$C_3F_{17}I$ (I)	$AlCl_3$	1:3	115-120, 24	$CF_3(CF_2)_6CCl_3$ (II)	55[3]
n-$C_{10}F_{21}I$ (V)	$AlCl_3$	1:3	115-120, 28	$CF_3(CF_2)_8CCl_3$ (VI)	55[3]
$I(CF_2)_4I$ (VII)	$AlCl_3$	1:6	115-120, 24	$Cl_3C(CF_2)_2CCl_3$ (VIII),	53
				$Cl_2C{=}CCl{-}CCl{=}CCl_2$ (IX)	26
n-$C_6F_{13}Br$ (X)	$AlCl_3$	1:3	175-180, 64	$CF_3(CF_2)_4CCl_3$ (XI),	47
				$CF_3(CF_2)_4CCl_2Br$ (XII),	13
				(X)	32
$(CF_3)_2CFO(CF_2)_4I$ (XIII)	$AlCl_3$	1:3.5	100-105, 63[4]	$(CF_3)_2CFO(CF_2)_3CCl_3$ (XIV)	43[3]
$(CF_3)_2CFO(CF_2)_2I$ (XV)	$AlCl_3$	1:3.5	100-105, 60[5]	$(CF_3)_2CFOCF_2CCl_3$ (XVI),	26
				$(CF_3)_2CFOCF{=}CCl_2$ (XVII)[6],	19
				$(CF_3)_2CFOCCl{=}CCl_2$ (XVIII),	19
				$(CF_3)_2CFOCCl_2CCl_3$ (XIX),	2
n-$C_8F_{17}I$ (I)	$AlBr_3$	1:1.5	75-80, 72	$CF_3(CF_2)_6CBr_3$ (XX)	56[3]

[1] In all reactions, dark intractible materials were formed. [2] Yields based on GC area percent unless indicated otherwise. [3] Isolated yield. [4] Minor products containing four and five chlorine atoms as well as degradation products like C_4Cl_6, $C_4F_4Cl_6$ were present. [5] Tetrachloroethylene (7%) and hexachloroethane (1%) were also identified. [6] Characterization based on MS data alone.

successfully used in Friedel-Crafts acylations using $AlCl_3$ at temperatures below 100°C without replacement of fluorine atoms alpha to the oxygen. However, reactions of these iodides with $AlCl_3$ at 100-105°C gave some polychlorinated products and degradation products. While these were formed only in small amounts in the reaction of XIII, a highly complex mixture of products was obtained from XV. (See experimental section)

The reaction of I with anhydrous $AlBr_3$ was also studied. Extensive charring of the reaction mixture was observed after the components were heated at 115-120°C in a pressure reactor for 24 h. The reaction products were extracted with diethyl ether, after hydrolysis of the crude reaction mixture and showed on GC/MS, the presence of $CF_3(CF_2)_6CBr_3$ (XX), $CF_3(CF_2)_6CHBr_2$, C_2HBr_5, C_2Br_4, C_2HBr_3 and CBr_4. The compounds containing hydrogen might be formed by the hydrolysis of intermediate perfluoroalkylaluminum species formed during the reaction. Heating I with 1.5 molar equivalents of $AlBr_3$ at a milder temperature of 75-80°C for 72 h led to isolation of the expected product, XX in 56 percent yield.

It appears from these observations that this reaction is general and may be represented as follows:



$$R_fCF_2X + AlX'_3 \longrightarrow R_f\text{-}\underset{X'}{\overset{X'}{C}}\text{-}X'$$

X = I, Br

X' = Cl,Br

R_f = Perfluoroalkyl, Perfluoroalkylether

Further studies on the $AlBr_3$ reaction as well as the use of other Lewis acids are in progress. The study is also being extended to sp^2 halides.

TABLE 2

^{19}F Chemical shifts of perfluoroalkyl compounds

Structure $R(CF_2)_nX$	X	^{19}F Chemical Shifts (ppm) Standard-$CFCl_3$						
		CF_3	CF_2	CF_2	$(CF_2)_n$	CF_2	CF_2	X
$CF_3(CF_2)_6CF_2I$ (I)	CF_2I	-82.3	-126.6	-122.4	$-(122.4)_2$	-122.4	-113.5	-58.6
$CF_3(CF_2)_6CCl_3$ (*II*)	CCl_3	-82.5	-127.0	-123.5	$-(122.5)_2$	-116.4	-110.0	
$CF_3(CF_2)_8CCl_3$ (VI)	CCl_3	-80.5	-125.7	-122.0	$-(121.1)_4$	-114.5	-110.4	
$CF_3(CF_2)_4CCl_2Br$ (*XII*)	CCl_2Br	-81.8	-126.6	-122.9		-114.8	-106.7	
$CCl_3(CF_2)_2CCl_3$ (VIII)	CCl_3				$-(101.9)_2$			

TABLE 3

^{19}F Chemical shifts of perfluoroalkylether compounds

Structure $(CF_3)_2CFORX$	X	^{19}F Chemical Shifts (ppm) Standard - $CFCl_3$					
		CF_3	CFO	OCF_2	CF_2	CF_2	X
$(CF_3)_2CFO(CF_2)_4I$ (XIII)	CF_2I	-81.8	-145.4	-81.8	-125.1	-113.9	-59.2
$(CF_3)_2CFO(CF_2)_3CCl_3$ (XIV)	CCl_3	-82.2	-145.4	-82.2	-119.4	-109.5	
$(CF_3)_2CFOCF_2CCl_3$ (XVI)	CCl_3	-81.8	-146.4	-81.4			
$(CF_3)_2CFOCCl_2CCl_3$ (XIX)	CCl_3	-79.5	-149.0				
$(CF_3)_2CFOCCl{=}CCl_2$ (XVIII)	CCl_2	-79.8	-139.8				

The ^{19}F NMR data of the perfluoroalkyl and perfluoroalkylether compounds are presented in Tables 2 and 3 respectively.

EXPERIMENTAL

The anhydrous $AlCl_3$ and $AlBr_3$ were commercial samples and were used without further purification. Boiling points of samples isolated by preparative GC were determined by Differential Thermal Analysis. Gas chromatographic analysis were carried out on a Perkin-Elmer Sigma 2B instrument using a 12' x 1/4" stainless steel column packed with three percent OV-1 on 80/100 Supelcoport. IR spectra were obtained on a Perkin-Elmer Model 683 Grating Spectrophotometer. ^{19}F NMR spectra were obtained on a Varian A56/60 spectrometer. Chemical shifts were measured from $CFCl_3$. Mass spectral analysis were carried out on a Finnigan 4021 mass spectrometer fitted with a Finnigan INCOS Data System operated in the electron impact Mode. No attempts were made to optimize yields.

General procedure for the reaction of iodides and bromides with anhydrous aluminum halides

A 500 ml stainless steel Parr pressure reaction vessel was flushed with dry nitrogen and charged with the anhydrous aluminum salt. Calculated amounts of the organic iodide or bromide were added and the vessel closed. It was then cooled in a Dry-Ice/isopropanol bath for about 1 h and was evacuated. The pressure vessel was then heated to the desired temperature with rocking and maintained at that temperature for the duration of the reaction.

The reactor was cooled to ambient temperature, and in the case of highly volatile products, connected to a vacuum pump through a series of two -78° traps, to collect the product. For less volatile products, the pressure vessel was opened and the contents hydrolyzed by careful addition to a mixture of ice and dil. HCl. The crude products were then extracted with diethyl ether and washed with aqueous sodium thiosulfate. GC/MS analyses were performed on the dried diethylether solution of products. The diethyl ether solution was passed through a column of alumina. Further purification was effected by distillation on a spinning band column or by recrystallization.

The complex mixture of products from reaction of XV and $AlCl_3$ was distilled to obtain fractions rich in individual components and samples for characterization were isolated by preparative gas chromatography. The results are summarized in Table 1.

$\underline{CF_3(CF_2)_6CCl_3}$ (II) [7]

Colorless liquid boiling at 64-65°C/5 mm. IR (capillary film) 1352 (m), 1305 (m), 1250-1120 (vs), 1095 (m), 1018 (m), 1005 (m), 880 (w), 835 (s), 635 (s) cm^{-1}. MS (EI) <u>m/e</u> 455, 453, 451 (M^+-Cl); 319 $(C_6F_{13})^+$, 269 $(C_5F_{11})^+$, 231 $(C_5F_9)^+$, 169 $(C_3F_7)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 100 $(C_2F_4)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Found: C, 19.91%, calculated for $C_8F_{15}Cl_3$: C, 19.71%.

$\underline{CF_3(CF_2)_8CCl_3}$ (VI) (NC)

White solid melting at 54°C. IR (KBr) 1367 (w), 1330 (w), 1250-1130 (vs), 1100 (m), 1040 (w), 1020 (w), 938 (w), 845 (s), 814 (m), 758 (s), 708 (w), 698 (w), 650 (m), 635 (m) cm^{-1}. MS (EI) <u>m/e</u> 555, 553, 551 (M^+-Cl); 331 $(C_7F_{13})^+$, 219 $(C_4F_9)^+$; 169

$(C_3F_7)^+$, 131 $(C_3F_5)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 100 $(C_2F_4)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Found: C, 20.45%, calculated for $C_{10}F_{19}Cl_3$; C, 20.44%.

$CCl_3CF_2CF_2CCl_3$ (VIII)

Colorless liquid. BP(DTA) 207.5°C. (lit. [8] B.P 209°C) IR (capillary film) 1268 (w), 1237 (m), 1180-1120 (vs), 1010 (s,sh), 970 (m), 860-800 (vs), 662 (vs) cm^{-1}. MS(EI) *m/e* 307, 305, 303, 301, 299 (M^+-Cl); 185, 183, 181, 179 $(C_2F_2CCl_3)^+$; 173, 171, 169, 167 $(CF_2CCl_3)^+$, 155, 153, 151 $(C_2F_3Cl_2)^+$; 136, 134, 132 $(C_2F_2Cl_2)^+$; 137, 135 $(CF_2CF_2Cl)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 87, 85 $(CF_2Cl)^+$, 86, 84, 82 $(CCl_2)^+$. Anal. Found: C, 14.23%, calculated for $C_4F_4Cl_6$: C, 14.26%.

$CF_3(CF_2)_4CCl_3$ (XI)

Colorless liquid. BP(DTA) 143°C (lit. [5] BP 143°C). IR (capillary film) 1342 (vs), 1285 (s), 1270-1120 (vs), 1100 (s), 1085 (s), 992 (s), 905 (w), 870-805 (s), 740 (w), 715 (m), 670 (s) cm^{-1}. MS (EI) *m/e* 355, 353, 351 (M^+-Cl), 219 $(C_4F_9)^+$, 169 $(C_3F_9)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 100 $(C_2F_4)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$.

$CF_3(CF_2)_4CCl_2Br$ (XII) (NC)

Colorless liquid. BP (DTA) 158°C. IR (capillary film) 1342 (vs), 1290 (s), 1270-1120 (vs), 1100 (s), 1082 (s), 992 (s), 960 (m), 905 (w), 870-780 (s), 730 (m), 715 (m), 670 (s) cm^{-1}. MS (EI) *m/e* 399, 397, 395 (M^+-Cl), 355, 353, 351 (M^+-Br), 219 $(C_4F_9)^+$, 169 $(C_3F_7)^+$, 165, 163, 161 $(CCl_2Br)^+$, 131 $(C_3F_5)^+$, 100 $(C_2F_4)^+$, 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Found: C, 16.64%, calculated for $C_6F_{11}Cl_2Br$: C, 16.67%.

$(CF_3)_2CFO(CF_2)_3CCl_3$ (XIV) (NC)

Colorless liquid boiling at 51°C/20 mm. IR (capillary film) 1355 (m), 1330-1100 (vs), 995 (s), 982 (vs), 953 (s), 848 (vs), 802 (m), 772 (w), 755 (w), 719 (vs), 660 (m), 647 (m), 622 (m) cm^{-1}. MS (EI) m/e 421, 419, 417 (M^+-Cl), 271, 269, 267 $(M-C_3F_7O)^+$, 169 $(C_3F_7)^+$, 155, 153, 151 $(C_2F_3Cl_2)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 100 (C_2F_4), 87, 85 $(CF_2Cl)^+$, 69 $(CF_3)^+$. Anal. Found: C, 18.54%, calculated for $C_7F_{13}Cl_3O$: C, 18.54%.

$(CF_3)_2CFOCF_2CCl_3$ (XVI) (NC)

Colorless liquid. BP (DTA) 111°C. IR (capillary film) 1425 (w), 1320-1100 (vs), 978 (vs), 888 (m), 835 (s), 758 (m), 710 (m), 655 (s), 615 (m) cm^{-1}. MS (EI) m/e 321, 319, 317 (M^+-Cl), 235 $(C_3F_7OCF_2)^+$, 173, 171, 169, 167 $(CF_2CCl_3)^+$, 169 $(C_3F_7)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 69 $(CF_3)^+$. Anal. Found: C, 17.37%, calculated for $C_5F_9Cl_3O$: C, 16.99%.

$(CF_3)_2CFOCCl{=}CCl_2$ (XVIII) (NC)

Colorless liquid. BP (DTA) 123°C. IR (capillary film) 1598 (s,sh), 1330-1100 (vs), 1078 (vs), 985 (vs), 960 (vs), 825 (s), 762 (w), 725 (m) cm^{-1}. MS (EI) m/e 320, 318, 316, 314 (M^+), 169 $(C_3F_7)^+$, 151, 149, 147, 145 $(OC_2Cl_3)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 114, 112, 110 $(OC_2Cl_2)^+$, 84, 82 $(CCl_2)^+$, 69 $(CF_3)^+$. Anal. Found: C, 19.24%, calculated for $C_5F_7Cl_3O$: C, 19.04%.

$(CF_3)_2CFOCCl_2CCl_3$ (XIX) (NC)

Colorless liquid BP (DTA) 173°C. IR (capillary film) 1790 (w), 1310-1100 (vs), 1000 (s), 965 (vs), 848 (m), 765 (m), 735 (m), 712(m), 650 (w), 615 (s) cm^{-1}. MS (EI) m/e 357, 355, 353, 351, 349 (M^+-Cl), 271, 269, 267 (M^+-CCl_3), 207, 205, 203, 201, 199 $(C_2Cl_5)^+$, 185 $(C_3F_7O)^+$, 170, 168, 166, 164 $(C_2Cl_4)^+$, 123, 121, 119, 117 $(CCl_3)^+$, 69 $(CF_3)^+$. Anal. Found: C, 15.50%, calculated for $C_5F_7Cl_5O$: C, 15.54%.

$\underline{CF_3(CF_2)_6CBr_3}$ (XX) (NC)

White solid melting at 46-47°C. IR (KBr) 1362 (w), 1315 (w), 1232 (vs), 1200 (vs), 1145 (vs), 1100 (w), 1020 (w), 1008 (w), 882 (w), 835 (w), 798 (w), 765 (m), 740 (w), 730 (w), 718 (w), 710 (m), 675 (w), 625 (m), 600 (w), 555 (w), 522 (w) cm^{-1}. MS (EI) m/e 543, 541, 539 (M^+-Br), 286, 284, 282, 280 $(CFCBr_3)^+$, 255, 253, 251, 249 $(CBr_3)^+$, 224, 222, 220 $(C_2F_2Br_2)^+$, 193, 191 $(C_3F_4Br)^+$, 181 $(C_4F_7)^+$, 169 $(C_3F_7)^+$, 131 $(C_3F_5)^+$, 119 $(C_2F_5)^+$, 69 $(CF_3)^+$. Anal. Found: C, 15.24%, calculated for $C_8F_{15}Br_3$: C, 15.47%.

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