# PERFLUORODIMETHYLKETENE AND PERFLUOROMETHACRYLIC ACID COMMUNICATION 1. HEXAFLUOROISOBUTYRYL CHLORIDES FROM FLUORINATED ETHERS

I. L. Knunyants, Yu. A. Cheburkov, and M. D. Bargamova
Institute of Heteroorganic Compounds, Academy of Sciences, USSR
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This is the first of a series of papers on the methods of preparation and the properties of fluorine-containing ketenes. The literature on this new class of organofluorine compounds is confined to a report of an attempt to prepare the simple difluoroketene, which was not isolated in the individual state [1]. As will be clear from our further discussions, in the synthesis of fluoro ketenes they are frequently accompanied by fluoro acrylic acids, and vice versa. This justifies the joint examination of their properties. The present paper is devoted to the synthesis of hexa-fluoroisobutyryl chlorides, which serve as starting substances for the preparation of perfluorodimethylketene and de-rivatives of perfluoromethacrylic acid. Two methods were used for the synthesis of these acid chlorides: the degradation of fluorinated ethers under the action of acidic reagents and the conversion of some acid halides into others by their reaction with aluminum halides.

It is known that, when heated with sulfuric acid [2] or aluminum chloride [3] or when treated at a sufficiently high temperature [4], ethers containing perhalogenated groups decompose with formation of alkyl halides and fluor-inated acid halides:

$$R_F CFXOR \rightarrow R_F COF \perp RX.$$

We extended these reactions to ethyl 2-hydroperfluoroisobutyl ether (I), ethyl perfluoroisobutenyl ether (II), and the halogenation products from the latter: ethyl 1,2-dichloroperfluoroisobutyl ether (III) and ethyl 1,2-dibromo-perfluoroisobutyl ether (IV):

$$(CF_3)_2 \underset{(II)}{CHCF_2OC_2H_5} (CF_3)_2 C = \underset{(III)}{CFOC_2H_5} (CF_3)_2 CXCFXOC_2H_5 \quad X = Cl \ (III) \ \text{and} \ Br \ (IV).$$

We succeeded in improving the conversion of ethers into acid halides by the use of sulfuric acid monohydrate in place of the concentrated acid [5]. This reduces the extent of the competing reaction, in which the difluoro- or fluorohalo-methylene group is hydrolyzed into carbonyl. From 1.2-dibromoperfluoroisobutyl ethyl ether, apart from the previously known [2] 1-bromohexafluoroisobutyryl fluoride, we isolated also the corresponding acid bromide:

$$(CF_3)_2 CBrCFBrOC_2H_5 \xrightarrow[100\%]{H_2SO_4} \xrightarrow[--]{(CF_3)_2 CBrCOF} + [C_2H_5Br]$$

$$(CF_3)_2 CBrCOBr + [C_2H_5F]$$

The reaction of 2-hydroperfluoroisobutyl ethyl ether with aluminum chloride led to a mixture of 2-hydrohexafluoroisobutyryl fluoride and chloride, evidently as a result of the preliminary exchange of a fluorine atom for chlorine in the difluoromethylene group with subsequent elimination of ethyl chloride or fluoride;

$$(CF_3)_2 CHCF_2 OC_2 H_5 \xrightarrow{AlCl_3} [(CF_3)_2 CHCFClOC_2 H_5] - \xrightarrow{(CF_3)_2 CHCOF} + C_2 H_5 Cl$$

The liberation of both alkyl halides confirmed this reaction mechanism, but did not exclude the possibility of exchange of fluorine for chlorine in the fluorocarbonyl group.

An analogous mixture was obtained also in the reaction of perfluoroisobutenyl ether with aluminum chloride; 1,2-dichloro- and 1,2-dibromoperfluoroisobutyl ethyl ethers reacted with aluminum chloride with formation of the corresponding 2-haloperfluoroisobutyryl halides:

$$(CF_3)_2 C = CFOC_2H_5 \xrightarrow{X_1} (CF_3)_2 CXCFXOC_2H_5 \xrightarrow{AlCl_3} (CF_3)_2 CXCOX$$
.  
  $X = Cl \text{ and } Br$ 

The conversion of acid fluorides into acid chlorides and bromides is readily effected by the action of aluminum halides:

# (CF<sub>3</sub>)<sub>2</sub> CXCOF AlY<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub> CXCOY

in which X = H, Y = Cl and Br; X = Cl, Y = Br; X = Br, Y = Cl. We investigated also the thermal decomposition of perfluoroisobutenyl methyl ether. Unlike the previously prepared perfluoroisobutenyl ethyl ether [6], at 400° the methyl ether decomposes in two directions, one of which leads to the formation of perfluorodimethylketene [bistri-fluoromethylketene]:

$$(CF_3)_2 C = CFOCH_3 - \left| \begin{array}{c} \rightarrow [CH_3F] + (CF_3)_2 C = CO & 20\% \\ \rightarrow [-CH_3 - ] + (CF_3)_2 CHCOF & 80\% \end{array} \right|$$

The boiling points of the hexafluoroisobutyryl halides synthesized in this work are listed in Table 1.

x	Y	b.p., °C	$\Delta t (\mathbf{X} = \mathbf{Cl} \rightarrow \mathbf{H}), ^{\bullet}\mathbf{C}$	x	Y	<sup>b.p.,</sup> °C	$\Delta t (X = Br \rightarrow Cl),$	x	Y	b.p., °C
H	F	33	1	Cl*	F	34	20	Br	F	54
H	Cl	54	15	Cl	Cl	70	20	Br	Cl	90
H	Br	67	19	Cl	Br	86	20	Br	Br	106

\*For the preparation of this compound see the next communication.

The table shows that as we pass from X = Br to X = Cl the difference in boiling point shows a surprising regularity and falls by exactly 20°, whereas as we pass from X = Cl to X = H the regularity is broken as a result of the appearance of a hydrogen bond. As would be expected, hydrogen bonding is most marked in the case of 2-hydrohexafluoroisobutyryl fluoride, in which a hydrogen bond is possible not only between hydrogen atoms and oxygen, but also between hydrogen atoms and fluorine.

#### EXPERIMENTAL\*

Reaction of Aluminum Chloride with Fluorine-containing Ethers. Aluminum chloride (2 g) and perfluoroisobutenyl ethyl ether (34 g) were cooled to - 78° and mixed. The mixture was warmed carefully to room temperature and then further to 100°, and in the course of this treatment 31.9 g of liquid distilled off into a trap. By the fractionation of this through a Podbielniak column we obtained 1.6 g of ethyl fluoride, b.p. from -35.5 to -31° and mol. wt. 50 (calculated, 48), 1.2 g of a fraction of b.p. from -31 to 10°, 2.4 g of ethyl chloride, b.p. 11.5-12° and mol. wt. 63.5 (calculated, 64.5), 10.8 g (27%) of 2-hydrohexafluoroisobutyryl fluoride, b.p. 33-36° †, and 7.6 g (22%) of 2-hydrohexafluoroisobutyryl chloride, b.p. 51-55° and  $n_D^{20}$  1.3085. The literature [7] gives: b.p. 57-59° (752 mm);  $n_{20}^{20}$  1.3086.

<sup>\*</sup> This work was carried out with the participation of the graduate Yu. V. Makarov.

<sup>†</sup> The literature [6] gives b. p. 31-33°.

In an analogous distillation of 2-hydroperfluoroisobutyl ethyl ether over aluminum chloride we obtained 2hydrohexafluoroisobutyryl fluoride in 24% yield and the acid chloride in 7% yield.

Analogously, from 15.6 g of 1,2-dibromoperfluoroisobutyl ethyl ethyl ethyl ethyl and 10.7 g of aluminum bromide we obtained 11.0 g (80%) of 2-bromohexafluoroisobutyryl bromide; b.p. 106° (747 mm);  $n_D^{20}$  1.3900;  $d_4^{20}$  2.1811. Found: C 14.48; F 33.42%.  $C_4F_6Br_2O$ . Calculated: C 14.20; F 33.68%.

Chlorine was passed into 23.8 g of perfluoroisobutenyl ethyl ether until the increase in weight was 8 g (the theoretical amount is 7.5 g). In the subsequent treatment of the reaction mixture with 14 g (0.1 mole) of aluminum chloride we obtained 12.7 g (48%, b ased on the unsaturated ether) of 2-chlorohexafluoroisobutyryl chloride; b. p. 69.5° (745 mm);  $n_D^{20}$  1.3345;  $d_4^{20}$  1.647. Found: C 19.21; F 46.80%. C<sub>4</sub>F<sub>6</sub>Cl<sub>2</sub>O. Calculated: C 19.27; F 45.80%. Anilide, m.p. 77-78° (from heptane). Found: C 39.19; H 2.11; F 36.59%. C<sub>10</sub>F<sub>6</sub>H<sub>6</sub>ClON. Calculated: C 39.26; H 1.96; F 37.31%.

Reaction of Sulfuric Acid with 1,2-Dibromoperfluoroisobutyl Ethyl Ethyl Ether. 16 g of the ether and 30 g of 100% sulfuric acid were mixed at -20°. The liquid that distilled off when the mixture was warmed was fractionated through a column. We obtained 3.7 g (32%) of 2-bromohexafluoroisobutyryl fluoride (b. p. 49-54° (746 mm); m.p. 11-14°;  $n_D^{20}$  1.3158\*) and 5.1 g (36%) of 2-bromohexafluoroisobutyryl bromide, b. p. 100-108°.

Reaction of Aluminum Halides with Hexafluoroisobutyryl Fluorides. A mixture of 40.5 g of 2-hydrohexafluoroisobutyryl fluoride and 55 g of aluminum bromide was heated in a flask, fitted with reflux condenser cooled to -20° and thermometer immersed in the liquid, until the temperature ceased to rise, after which the reaction product was distilled from the reaction mixture. We obtained 44.8 g (86%) of  $\alpha$ -hydrohexafluoroisobutyryl bromide; b.p. 67-67.5° (741 mm);  $n_{20}^{20}$  1.3350;  $d_4^{20}$  1.8127. Found: Br 30.84%. C<sub>4</sub>HF<sub>6</sub>BrO. Calculated: Br 30.88%.

In an analogous way we synthesized the substances listed in Table 2.

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Product	Starting compound	Yield, %	Constants
(CF <sub>3</sub> ) <sub>2</sub> CHCOCl	(CF <sub>3</sub> ) <sub>2</sub> CHCOF	78	Similar to those described in [7]
(CF <sub>3</sub> ) <sub>2</sub> CClCOBr	(CF₃)₂CClCOF	74	B.p $8686,5^{\circ}$ (755 mm); $n_D^{20}$ 1,3608; $d_4^{20}$ 1,8760. Found: Br 27, 20 %; Calculated:Br 27,25 %.
(CF₃)₂CBrCOCl	(CF3)2CBrCOF	89	B.p. 90—91°; m.p. 0°; $n_D^{20}$ 1,3613; $d_4^{20}$ 1,9258. Found: Cl 12,01 %; Calculated: Cl 12, 09 %.
(CF <sub>3</sub> ) <sub>2</sub> CBrCOBr	(CF <sub>3</sub> ) <sub>2</sub> CBrCOF	73	Similar to those described above

TABLE 2

<u>Pyrolysis of Perfluoroisobutenyl Methyl Ether.</u> The reaction was carried out in the previously described apparatus [6]. In the pyrolysis of 82 g of the ether at 200-400° we obtained 65 g of pyrolyzate, in the fractionation of which through a Podbielniak column we isolated 15 g (22%) of perfluorodimethylketene, b.p. 5-6°. Found: C 27.46; H 0.95; F 63.12%; mol.wt. 181.  $C_4F_6O$ . Calculated: C 26.97; F 64.04%; mol.wt. 178.

The residue remaining after the distillation of perfluorodimethylketene was hexafluoroisobutyryl fluoride, which came over in the range 32-40°. Yield 33 g (43%). Perfluorodimethylketene is extremely hygroscopic and, when allowed to stand in air, is converted quantitatively into 2-hydrohexafluoroisobutyric acid, m.p. 56°, undepressed by admixture of a known sample.

<sup>\*</sup> The literature [2] gives: b.p. 54°; n<sub>D</sub><sup>20</sup> 1.3170.

## SUMMARY

1. When the appropriate ethers containing fluorinated groups react with sulfuric acid or aluminum halides, 2-hydro- and 2-halo-hexafluoroisobutyryl halides are obtained.

2. It was shown that in the fluorocarbonyl group of the acid fluorides obtained fluorine can be smoothly replaced by chlorine or bromine by the action of the appropriate aluminum halide.

3. Perfluorodimethylketene is formed in the pyrolysis of perfluoroisobutenyl methyl ether.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.