A New Synthesis of Fluorinated Oxetanes†

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Polyfluorinated oxetanes are prepared in high yields by an electrophilic [2 + 2] cycloaddition reaction between hexafluoroacetone and fluorinated ethylenes that is catalyzed by an anhydrous aluminum chlorofluoride Lewis acid. The reaction is regiospecific with hydrofluoroethylenes $CHX{=}CF_2$ (X = H, F, Cl, Br), whereas halotrifluoroethylenes $CFX{=}CF_2$ (X = Cl, Br) give nearly equal amounts of the isomeric oxetanes. Hexafluoropropylene oxide, which rapidly rearranges under the reaction conditions, can be substituted for hexafluoroacetone in this new oxetane synthesis.

Introduction

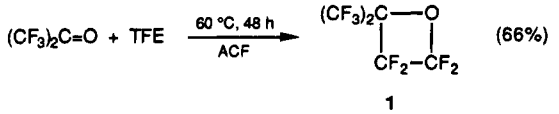
(Polyfluoro)oxetanes having high chemical and thermal stability[1] have been prepared by various methods, but the most common one involves the photoinitiated cycloaddition of ketones,[2a,b] aldehydes,[2b] and acyl fluorides[2a,c] to fluoroolefins. Other methods of preparation with more limited scope include intramolecular nucleophilic cyclization of fluorinated β-halo alcohols $R_2C(OH)CF_2CHClF$[3] and replacement of halogen in CH_2X groups of 2- and 3-(halomethyl)oxetanes by reaction with alkoxides of fluoro alcohols.[4] Another approach to oxetanes with perfluoroalkyl groups is the intramolecular cyclization of 2-perfluoroalkyl 1,3-diols in H_2SO_4, but yields are low.[5] The highly electrophilic hexafluoroacetone and some chloropoly(fluoro)acetones can form four-membered cyclic ethers with very electron-rich vinyl[6] or propargyl[7] ethers without a catalyst.

The formation of 2,2,3,3-tetrafluorooxetane as a low-yield byproduct in the electrophilic condensation of tetrafluoroethylene (TFE) with paraformaldehyde in hydrogen fluoride[8] was first reported by Weinmayer in 1963. This approach was later used to prepare some partially fluorinated oxetanes from perfluorovinyl ethers,[9,10] although the reactions are unselective and give poor yields. Antimony pentafluoride promotes the reaction of 1,1,3-trichlorotrifluoroacetone with TFE or trifluoroethylene to produce a difficult-to-separate mixture of chlorofluoropentan-2-ones and oxetanes,[11] but hexafluoroacetone and 1,3-dichlorotetrafluoroacetone fail to react under similar conditions.[12]

In marked contrast with the moderately active $AlCl_3$ but inert AlF_3, the recently introduced Lewis acid aluminum chlorofluoride (ACF), $AlCl_xF_y$, is an extremely effective catalyst for the condensation of halomethanes[13] and some fluoroolefins[14] with fluoroethylenes. It is readily generated by reacting $AlCl_3$ with fluorinated materials such as $CFCl_3$, $CHCl_2F$, or $CF_3CF{=}CF_2$.[13,14] As a moisture sensitive but easily handled solid that does not fluorinate double bonds of olefins 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.[12] It, for example, effectively catalyzes the condensations of perfluoropent-2-ene and perfluorocyclopentene with TFE,[14] which fail when SbF_5 is used.[12] This paper describes the use of ACF to promote electrophilic [2 + 2] cycloadditions of hexafluoroacetone with various fluoroethylenes to provide a useful, easy-to-scale synthesis of polyfluorinated oxetanes.

Results and Discussion

Hexafluoroacetone (HFA) in the presence of ACF reacts with TFE to form perfluoro-2,2-dimethyloxetane (**1**), isolated in 66% yield (96–100% yield based on converted HFA). Poly(tetrafluoroethylene) (PTFE) is the only



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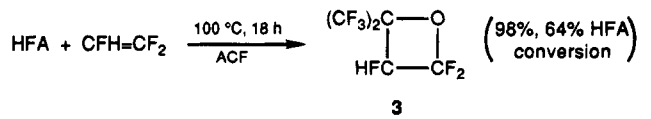
byproduct formed. In contrast to the photochemical reaction,[15] HFA and trifluoroethylene (**2**) react regiospecifically to give only 3*H*-perfluoro-2,2-dimethyloxetane (**3**) in almost quantitative yield based on converted HFA (64%). The formation of this particular regioisomer is



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consistent with an electrophilic process, since electro-

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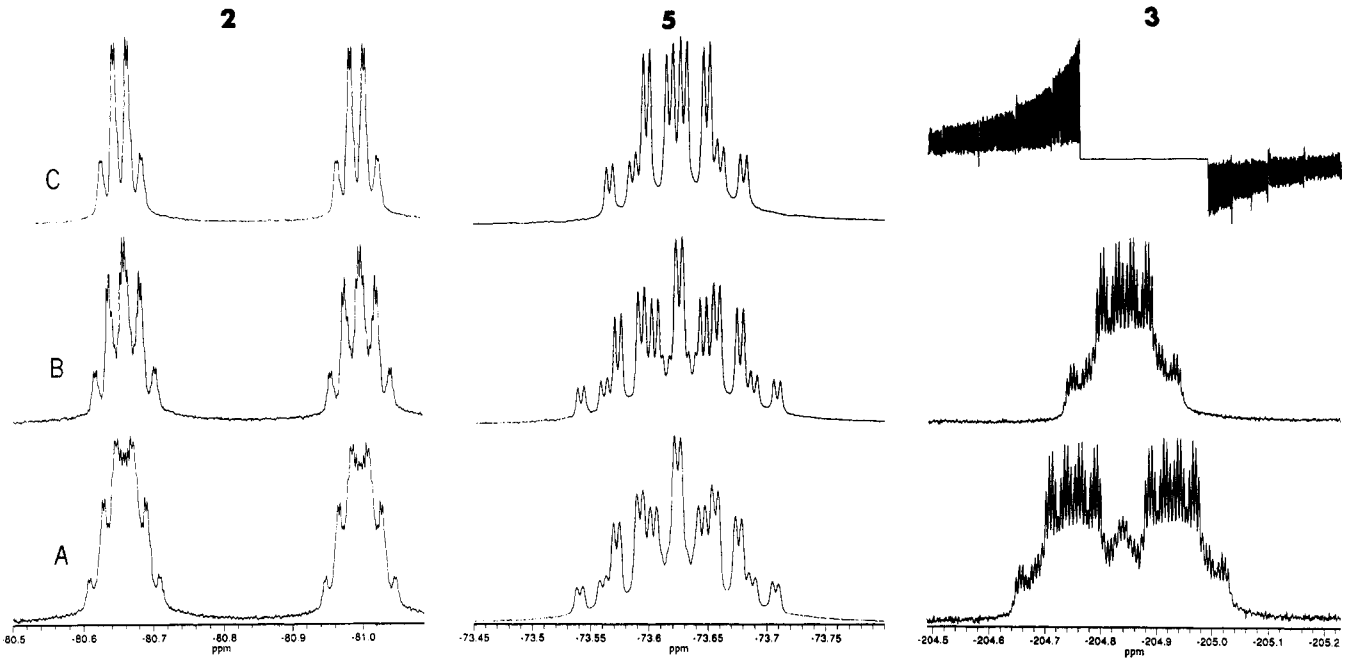
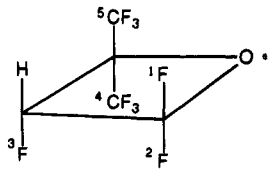


Figure 1. (A, bottom) ^{19}F spectrum of oxetane **3**. (B, middle) ^{19}F $\{^1H\}$ spectrum of **3**. (C, top) ^{19}F $\{^1H\}$ {selective ^{19}F} spectrum of **3**. Numbers on top represent fluorine positions given in Table 1.

Table 1. ^{19}F NMR Chemical Shifts and Coupling Constants for Oxetane 3

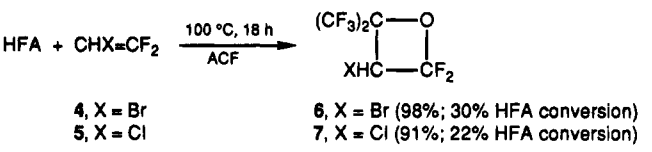


entry	chemical shifts (ppm)	coupling constants (Hz) $J_{F\text{-}F}$	$J_{H\text{-}F}$
1	−66.51	$J_{(1\text{-}2)} = 95.9$ $J_{(1\text{-}3)} < 0.5$ $J_{(1\text{-}4)} = 1.6$ $J_{(1\text{-}5)} = 1.1$	$J_{(H\text{-}1)} = 0.6$
2	−80.83	$J_{(2\text{-}3)} = 6.9$ $J_{(2\text{-}4)} = 5.6$ $J_{(2\text{-}5)} = 1$	$J_{(H\text{-}2)} = 4.0$
3	−204.84	$J_{(3\text{-}4)} = 14.9$ $J_{(3\text{-}5)} = 1.5$	$J_{(H\text{-}3)} = 50.4$
4	−73.62	$J_{(4\text{-}5)} = 8.9$	$J_{(H\text{-}4)} = 0.5$
5	−77.83		$J_{(H\text{-}5)} < 0.5$

philes preferentially attack at the CFH group of trifluoroethylene.[12,16]

The structures of all oxetanes were determined by IR, MS, and ^{19}F and ^1H NMR spectroscopic data. Chemical shifts and coupling constants for **3** (Table 1) were established by a combination of broad-band proton decoupling and selective fluorine decoupling NMR experiments (see Experimental Section and Figure 1). The assignments are based on NMR data reported for 2-(fluoroalkyl)-3,4-difluorooxetanes,[17] assuming that the chemical shifts of fluorine on the C-4 carbon of the ring *cis* to hydrogen occur at lower field and that $^4J_{CF_3\text{-}F}(cis) > {}^4J_{CF_3\text{-}F}(trans)$. The parameters found for compound **3** are given in Table 1.

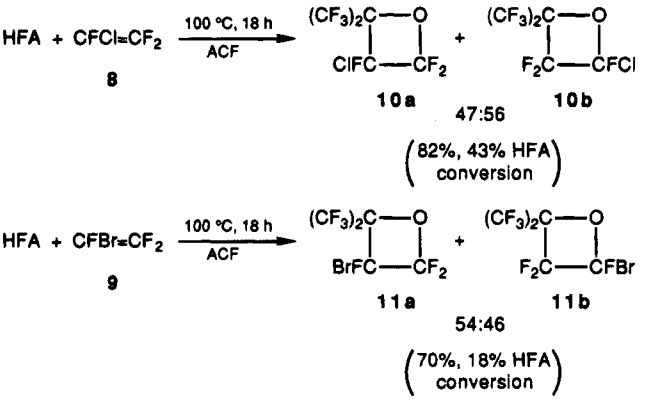
2-Bromo-1,1-difluoroethylene (**4**) and 2-chloro-1,1-difluoroethylene (**5**) similarly react with HFA to give oxetanes **6** and **7**, respectively, in high yields. Electrophilic addition reactions to chlorotrifluoroethylene (**8**) and bromotrifluoroethylene (**9**), however, usually are not



4, X = Br
5, X = Cl

6, X = Br (98%; 30% HFA conversion)
7, X = Cl (91%; 22% HFA conversion)

regioselective and produce almost equal amounts of both isomers.[12,16] Not surprisingly, therefore, the reactions of **8** and **9** with HFA afford both isomers of oxetanes **10** and **11**, respectively. In the case of **8**, the reaction mixture also contained about 10% of 1,2-dichlorohexafluorocyclobutane (**12**), which probably arose from the thermal cyclodimerization of **8**. Despite the moderate HFA



conversions in some instances, these cycloadditions are very clean, and simply removing unreacted starting material affords crude product of 96–98% purity.

HFA reacts with vinylidene fluoride (**13**) to give mainly oxetane **14**, accompanied by alcohols **15** and **16**. Pure oxetane **14** was isolated in about 80% yield by fractional distillation or washing the reaction mixture with 5–10% aqueous NaOH.

The amount of alcohols **15** and **16** formed in the reaction is not particularly sensitive to temperature wherein the same ratio of **14**–**16** resulted at 50 and 100 °C. In a separate experiment, pure **14** did not isomerize in the presence of ACF after 24 h at 120 °C, which implies

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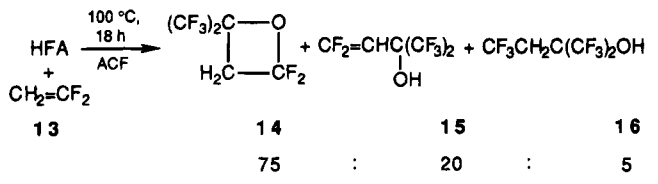
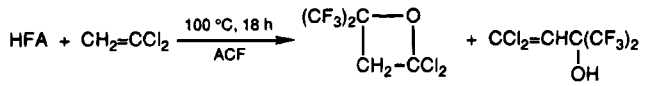


15 is a primary reaction product. A possible reaction mechanism is shown in Scheme 1.

Coordination of ACF with the carbonyl group of HFA produces charged complex **17**, which can regioselectively attack **13** to generate zwitterion **18**. This intermediate then principally cyclizes intramolecularly to oxetane **14** but also can undergo some competitive 1,3 proton shift to form byproduct **15**. Alcohol **16** probably forms via addition of HF to **15**, although the source of hydrogen fluoride, other than adventitious moisture, is unclear.

The reaction of HFA and 1,1-dichloroethylene (**19**) likewise gives a mixture of chlorooxetane **20** and alcohol **21**. Both compounds have been made previously by reacting **14** with $AlCl_3$.[15] However, olefin **19** was the only



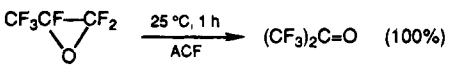
The yield of **20** 91%, conversion of HFA 19%.

chloroolefin reactive toward HFA. Chloroolefins such as tetrachloroethylene and trichloroethylene failed to react with HFA at 100 °C in the presence of ACF.

Hexafluoroacetone is much more active in these cycloadditions than other halofluoro ketones. For instance, monochloropentafluoroacetone reacts with TFE (60 °C, 18 h) and CH_2=CF_2 (100 °C, 18 h) to give the corresponding oxetanes in only 10–20% yields, and the product from CH_2=CF_2 is heavily contaminated with byproducts.

ACF is by far the most active catalyst for cycloaddition. Under similar conditions (100 °C, 18 h), the reaction of HFA with CHF=CF_2 in the presence of $AlCl_3$ produces the corresponding oxetane in 8% yield, and barely trace amounts of **3** are observed when NbF_5 is used as a catalyst.

Strong Lewis acids such as SbF_5 are known to rapidly convert hexafluoropropene oxide (HFPO) into HFA under mild conditions.[18] ACF also very efficiently catalyzes this rearrangement, which proceeds at room temperature, can be carried out in either an open or a closed system, and produces HFA in quantitative yield. These results



indicate HFPO can be used as an *in situ* source of HFA under the conditions for electrophilic cycloaddition. In fact, HFPO reacts with TFE or trifluoroethylene under the same conditions used with HFA to afford **1** (95% yield) or **3** (75% yield).

Experimental Section

^{19}F and ^1H NMR spectra were recorded on a QE-300 (General Electric) instrument using $CFCl_3$ as an internal standard and $CDCl_3$ as a lock solvent. The ^{19}F, ^{19}F $\{^1H\}$, and

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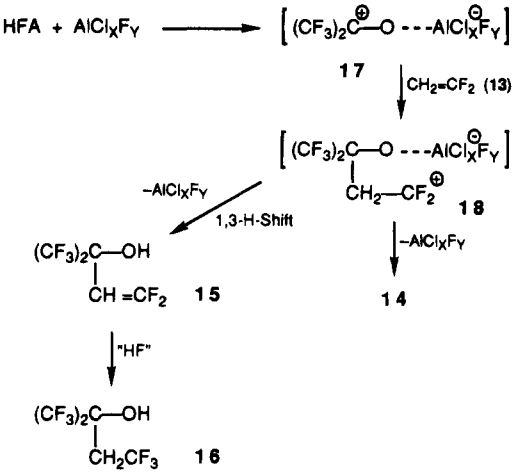
Scheme 1



^{19}F $\{^1H\}$ {selective ^{19}F} spectra of compound **3** were recorded on a GE Omega 300 WB system, equipped with two broadband decoupler channels (designated f2 and f3) and used a standard ^{19}F $\{^1H\}$ probe (the braces indicate the nuclei being decoupled). These experiments were acquired at 282.75 MHz using a sweep width of 86 956 Hz; a 90° pulse width of 8 μs, and a block size of 128K, which was zero-filled twice prior to Fourier transformation, and were referenced external to Freon 11 ($CFCl_3$). The ^{19}F $\{^1H\}$ experiment was performed using a standard inverse gated decoupling sequence with Waltz-16 decoupling. Since we could not find any literature references describing the procedures necessary to perform a ^{19}F $\{^1H\}$ {selective ^{19}F} experiment, the details of this experiment are given below.

The ^{19}F $\{^1H\}$ {selective ^{19}F} experiment was run using the same sequence as the ^{19}F $\{^1H\}$ experiment except the pulse sequence was extended to include f3 homonuclear cw decoupling during the acquisition and, using the f3 decoupler format on the GE system, the f3 pulse width (f3-w) and f3 postdelay (f3-y) were set to 4 and 3 μs to prevent receiver overload.

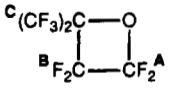
Hardware Setup to Perform the ^{19}F $\{^1H\}$ {Selective ^{19}F} Experiment. ^{19}F {selective ^{19}F} part of the ^{19}F $\{^1H\}$ {selective ^{19}F} experiment was carried out as follows. (a)The observed frequency (282.75 MHz) was combined with f3 decoupler (whose frequency was set up to irradiate the fluorine resonance at −204.8 ppm in the fluorine spectrum) via a high-band directional coupler, whose output was connected to the input of the probe interface module. (b) The output of the probe interface module (called transmitter/receiver port) was then passed through a duplexer, tuned to 282.75 MHz, and connected to the observed connector on the probe. The proton decoupling portion of the ^{19}F $\{^1H\}$ {selective ^{19}F} experiment was carried out by passing the f2 decoupler, whose frequency was set at 5 ppm in the proton spectrum (300.75 MHz), through a duplexer tuned to 300.75 MHz, and into the decoupler input of the probe.

IR spectra were recorded on Perkin-Elmer Model 983G spectrometer in the gas phase or using CH_2Cl_2 as a solvent. The aluminum chlorofluoride was prepared by the literature procedure[14] and stored in a drybox. Proper handling of the catalyst is critical, since it is extremely sensitive to atmospheric moisture. Yields of oxetanes are based on converted HFA. Compounds **20** and **21**[15] were identified by comparison of ^{19}F NMR, IR, and mass spectral data with literature values.

Procedures for the Preparation of Fluorooxetanes. *Caution: Hexafluoroacetone is toxic and should be handled in a well-ventilated hood to avoid contact with its vapors.*

Method A (Reaction with TFE). A 400-mL Hastelloy shaker tube was loaded with 5 g of freshly prepared ACF, 70 g (0.42 mol) of HFA, and 20 g (0.2 mol) of TFE. After shaking at 60 °C for 24 h, a second portion of TFE (20 g) was added. After another 24 h at 60 °C, gaseous products were bled out of the reaction vessel and collected in a −78 °C trap. Unreacted HFA was distilled from this mixture on a low-temperature distillation column. The remaining liquid was washed with cold water to remove residual HFA, dried over P_2O_5, and

distilled. The 10 g of white solid residue remaining in the shaker tube after washing with water was identified by IR as poly(TFE). There was isolated 70 g (yield 66%, 100% based on converted HFA, 65% conversion of HFA) of perfluoro-2,2-dimethyloxetane (**1**): bp 26-27 °C (lit.[1] bp 27 °C); IR (gas) 1400 (s), 1321 (vs), 1295 (m),1248 (s), 1195 (m), 1175 (m), 1109 (s), 1036 (s), 989 (m), 884 (m), 763 (m), 726 (m), 669 (w) cm^{-1}; GC/MS *m/e* 265.9785 (M^+, $C_5F_{10}O^+$, calcd 265.9789); ^{19}F NMR ($CDCl_3$) δ −72.98 (t, $6F_C$), −118.79 (hept, J_{AB} = 9 Hz, $2F_B$), −79.70 (brs, $2F_A$).

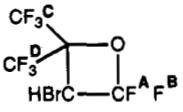


In the reaction of HFPO with TFE under similar conditions, the yield of **1** was 96% based on 100% conversion of HFPO, 70% HFA recovered, and 38% TFE conversion.

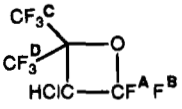
Method B (General procedure). A 400-mL Hastelloy shaker tube was loaded with 2−5 g of ACF, cooled to −78 °C, evacuated, and charged with 0.3−0.4 mol of HFA and an equimolar amount of haloalkene. The reaction vessel was shaken at 100 °C for 18 h. The reaction mixture was bled out of the reactor at 40−50 °C and collected in a cold trap (−78 °C). Starting materials were distilled out using a low-temperature distillation column, and the residue was washed with cold water to remove any residual HFA, dried over P_2O_5, and distilled.

3*H*-Perfluoro-2,2-dimethyloxetane (3): from HFA and trifluoroethylene (64% isolated yield, 98% on converted HFA, 64% HFA conversion); bp 44-45 °C; IR (gas) 3020 (CH, w), 1501 (w), 1416 (s), 1250 (vs), 1193 (s),1147 (s), 1092 (s), 1035 (s), 988 (m), 870 (m),789 (w), 747 (m), 722 (w), 684 (m) cm^{-1}; GC/MS *m/e* 247.9885 (M^+, $C_5HF_9O^+$, calcd 247.9883). NMR data for **3** are given in Table 1.

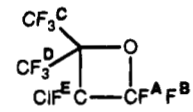
3-Bromo-3*H*-perfluoro-2,2-dimethyloxetane (6): from HFA and 2-bromo-1,1-difluoroethylene (98% yield, 30% HFA conversion); bp 77−78 °C; IR (gas) 3034 (w), 1342 (vs), 1305 (vs), 1242 (vs), 1181 (s), 1163 (s), 1127 (s), 1091 (s), 1025 (s), 966 (s), 796 (m), 759 (m), 745 (m), 697 (m), 653 (m) cm^{-1}; GC/MS *m/e* 288.8880 ([M − F]$^+$, $C_5HBrF_7O^+$, calcd 288.8854); ^{19}F NMR δ −59.32, −68.73 (ABm, J_{AB} = 88 Hz, 2F; F_A dd, J_{HA} = 5 Hz; F_B dp, J_{HB} = 10 Hz), −72.92 (dq, J_{CD} = 10 Hz, $3F_C$), −76.82 (q, *J* = 10 Hz, $3F_D$); ^1H NMR δ 5.25 (t, *J* = 5, 10 Hz). Anal. Calcd for C_5HBrF_8O: C, 19.44; F, 49.19. Found: C, 19.41; F, 48.76.



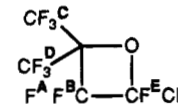
3-Chloro-3*H*-perfluoro-2,2-dimethyloxetane (7): from HFA and 2-chloro-1,1-difluoroethylene (91% yield, 22% conversion of HFA); bp 62−65 °C; IR (main) 3009 (C-H, w), 1338 (m), 1304−1086 (CF) cm^{-1}; GC/MS *m/e* 263.9540 (M^+, $C_5HClF_8O^+$, calcd 263.9588); ^{19}F NMR δ −60.28, −73.64 (ABm, J_{AB} = 87 Hz, 2F; F_A dd, J_{HA} = 5 Hz; F_B dp, J_{HB} = 9 Hz), −72.68 (dqd J_{CD} = 6 Hz, $3F_C$), −76.93 (q, *J* = 6 Hz, $3F_D$); ^1H NMR δ 5.50 (dd, *J* = 5, 9 Hz).



3- and 4-Chloroperfluoro-2,2-dimethyloxetane (10a,b): from HFA (0.3 mol) and chlorotrifluoroethylene (**8**) (0.3 mol) with 3 g of ACF was isolated 37 g of liquid, bp 55 °C, containing 42% **10a** + 48% **10b** (lit.[1] bp 55−56 °C) (82% yield, 43% conversion of HFA, 48% conversion of **8**) and 10% 1,2-dichloroperfluorocyclobutane by GC, NMR, and IR (mixture, gas) 1345 (s), 1316−1007 (C-F) cm^{-1}; GS/MS (mixture of isomers) *m/e* 281.9449 (M^+, $C_5ClF_9O^+$, calcd 281.9494); ^{19}F NMR (mixture) **10a** δ −71.64, −76.74 (ABm, J_{AB} = 85 Hz, 2F; F_A d, F_B dd), −71.84 (m, $3F_C$), −73.05 (m, $3F_D$), −124.73 (m, $1F_E$); **10b** δ −108.95, −115.47 (ABm, J_{AB} = 204 Hz, 2F; F_A d; F_B dm), −72.42 (m, $3F_C$), −72.64 (m, $3F_D$), −61.38 (s, $1F_E$).

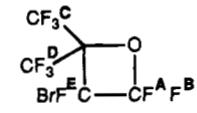


10a

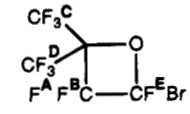


10b

3- and 4-Bromoperfluoro-2,2-dimethyloxetane (11a,b): from HFA and bromotrifluoroethylene; 54:46 **11a:11b** by GC and NMR (70% yield, 18% conversion of HFA); bp 67−68 °C (lit.[1] bp 70−71 °C); IR (gas, mixture of isomers) 1339 (vs), 1242 (vs), 1199 (s), 1170 (s), 1149 (s), 1089 (vs), 1056 (s), 1030 (s), 1000 (s), 950 (m), 815 (m), 756 (m), 724 (m) cm^{-1}; GC/MS (mixture of isomers) *m/e* 306.8998 ([M − F]$^+$, $C_5BrF_8O^+$, calcd 306.9005); ^{19}F NMR (mixture) **11a** δ −66.60, −72.32 (ABm, J_{AB} = 83 Hz, 2F; F_A d; F_B dd), −71.32 (m, $3F_C$), −72.94 (m, $3F_D$), −125.34 (m, $1F_E$); **11b** δ −103.82, −115.47 (ABm, J_{AB} = 201 Hz, 2F; F_A d; F_B dm), −72.30 (m, $3F_C$), −72.74 (m, $3F_D$), −54.48 ($1F_E$). Anal. Calcd for C_5BrF_9O: C, 18.36. Found: C, 18.52.



11a



11b

3,3-Dihydroperfluoro-2,2-dimethyloxetane (14): from HFA (0.3 mol), 1,1-difluoroethylene (0.25 mol), and 5 g of ACF at 100 °C for 18 h was isolated 25 g of crude product containing 75% **14**, 20% **15**, and 5% **16** by ^{19}F NMR. Pure **14** (82% yield, 33% conversion of HFA), bp 55−55.5 °C, and a 65:35 mixture of **15** and **16** (bp 71−73 °C) were isolated by spinning-band distillation. **14**: IR (gas) 1437 (w), 1341 (vs), 1309 (s), 1228 (s), 1209 (s), 1159 (m), 1104 (s), 1083 (m), 1023 (m), 935 (m), 844 (m), 724 (w), 692 (w) cm^{-1}; GC/MS *m/e* 210.9986 ([M − F]$^+$, $C_5H_2F_7O^+$, calcd 210.9994); ^{19}F NMR δ −72.28 (brs, 6F), −60.25 (tm, 2F); ^1H NMR δ 3.46 (t, J_{HF} =7 Hz) (lit.[2c] ^1H NMR 3.41 ppm, *J* =7 Hz). **15**: IR (liq, in mixture) 3353 (OH), 1753(C=C) cm^{-1}; GC/MS (in mixture) *m/e* 229.9984 (M^+, $C_5H_2F_8O^+$, calcd 229.9978); ^{19}F NMR $F^BF^CC{=}CHC(CF_3^A)_2OH$ δ −79.14 (d, J_{AB} = 4.5 Hz, 6F), −72.68, −74.26 (AB m, J_{BC} = 20 Hz, 2F; F_B = dd, J_{AB} = 4.5 Hz, J_{HB} =23 Hz; F_C dm, J_{HC} = 3 Hz); ^1H NMR δ 3.22 (brs, OH), 4.58 (dd, *J* = 23, 3 Hz, 1H). **16**: GC/MS (in mixture) *m/e* 231.0054 ([M − F]$^+$, $C_5H_3F_8O^+$, calcd 231.0056); ^{19}F NMR δ −77.96 (m, 6F), −60.40 (m, 3F); ^1H NMR δ 2.84 (q, J_{HF} = 9 Hz, 2H), 3.28 (brs, OH).

In the reaction of $CH_2{=}CF_2$ with HFPO under similar conditions, oxetane **14** was isolated in 75% yield; conversion of HFA was 23%.

Reaction of HFA with $CH_2{=}CCl_2$. From HFA (0.3 mol), 1,1-dichloroethylene (0.3 mol), and 5 g of ACF at 100 °C for 18 h was isolated 16 g of liquid with bp 100−103 °C which was, according to GC/MS and ^1H and ^{19}F NMR, a mixture of 90% 2,2-bis(trifluoromethyl)-4,4-dichlorooxetane (**20**) and 10% 3-hydroxy-3,3-bis(trifluoromethyl)-1,1-dichlorobut-1-ene (**21**). Calculated yield of oxetane was 91%; the conversion of HFA was 19%.

Isomerization of HFPO. Hexafluoropropylene oxide (50 mmol) and 1 g of ACF were placed in a stainless steel cylinder at 25 °C. After 1 h, all the HFPO was converted into hexafluoroacetone according to IR (gas phase). The selectivity was 100%, 96% isolated yield.

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