JOC Article

Preparation of Highly Fluorinated Cyclopropanes and Ring-Opening Reactions with Halogens†

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Various highly fluorinated cyclopropanes **1** were prepared by reaction of the appropriate fluorinated olefins with hexafluoropropylene oxide (HFPO) at 180 °C. The fluorinated nitrile **1e** was converted to the triazine derivatives **2a** and **2b** by catalysis with Ag_2O and $NH_3/(CF_3CO)_2O$, respectively. The fluorinated cyclopropanes reacted with halogens at elevated temperatures to provide the first useful, general synthesis of 1,3-dihalopolyfluoropropanes. At 150−240 °C, hexafluorocyclopropane and halogens X_2 produce $XCF_2CF_2CF_2X$ (X = Cl, Br, I) in 50−80% isolated yields. Pentafluorocyclopropanes *c*-C_3F_5Y [Y = Cl, OCF_3, OC_3F_7 and $OCF_2CF(CF_3)OCF_2CF_2Z$; Z = SO_2F, CN, CO_2Me] react regiospecifically at 150 °C to give XCF_2CF_2CFXY, *c*-C_3F_5Br reacts regioselectively with Br_2 to give a 16.7:1 mixture of $BrCF_2CF_2CFBr_2$:$BrCF_2CFBrCF_2Br$, whereas *c*-C_3F_5H reacts unselectively with I_2 to produce a statistical 2:1 mixture of ICF_2CF_2CFHI:ICF_2CFHCF_2I. Tri- and di(pentafluorocyclopropyl) derivatives **2** also undergo ring-opening reaction with halogens to give **16** and **17**. Upon treatment of tetrafluorocyclopropanes **1j**, **1k**, and **1l** with Br_2 or I_2, ring opening occurred exclusively at substituted carbons to give $XCF_2CF_2CXY_2$. Thermolysis of the ring-opened product $ICF_2CF_2CFIOR_F$ at 240 °C gave R_FI and ICF_2CF_2COF in high yields.

Introduction

Perfluoroalkyl iodides are the most widely used fluorinated building blocks for introducing perfluoroalkyl groups into organic molecules. These iodides are prepared mainly through telomerization of short-chain perfluoroalkyl iodides such as CF_3I and C_2F_5I with tetrafluoroethylene.[1] Although perfluoroalkylene diiodides have recently been reported to be excellent telogens for the synthesis of fluorinated thermoplastic elastomers and other materials, preparation of the starting materials is difficult and overall yields are low.[2] The telomerization of ICF_2CF_2I and tetrafluoroethylene yields the desired diiodides along with significant amounts higher oligomers.[2e] The diiodides with an odd number of CF_2's are even more difficult to prepare and require expensive starting materials and tedious experimental procedures.[3] Reaction of halodifluoroacetate with iodine and CuI provided the first practical method for the preparation of CF_2I_2.[4a] We have developed a facile method for the preparation of 1,3-diiodofluoropropane derivatives by ring-opening reaction of fluorinated cyclopropanes with iodine and difluorodiiodomethane and by nickel-catalyzed reaction of perfluoroepoxide with iodine.[4b,c] The ring-opening reaction could be readily extended to make other fluorinated 1,3-dihalides by reaction of fluorinated cyclopropanes with the corresponding halogens. More interestingly, I have found the ring-opening reaction can be used to make tri-, tetra-, and hexaiodides, which could not be made by other means. Herein, I report my detailed results of the preparation of highly fluorinated cycloproanes and their reactions with halogens.

Results and Discussion

I. Preparation of Fluorinated Cyclopropanes 1. Fluorinated cyclopropanes **1** are usually prepared by the addition of a difluorocarbene to the appropriate alkenes.[5] Although there are a number of sources to produce the difluorocarbene, we used hexafluoropropylene oxide (HFPO) as a carbene precursor since HFPO is a commercial product and the byproduct CF_3COF is readily separated from the product and is useful for making other fluoromonomers. In addition, the difluorocarbene from HFPO is highly reactive to fluorinated alkenes and in most cases gives the fluorinated cyclopropanes in high yields.[6] Hexafluorocyclopropane can be readily prepared by heating HFPO at 180−185 °C. Other substituted cyclopropanes were made by heating a mixture of HFPO

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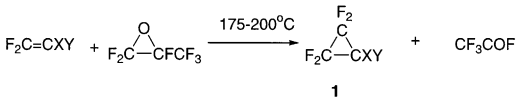
with the appropriate fluorinated alkenes as shown in the Table 1. Although 1 equiv of HFPO should theoretically be sufficient, a slight excess of HFPO gave higher yields of the desired cyclopropanes. Various other perfluorovinyl ethers also gave cyclopropane derivatives **1b**−**f** in high yields. The perfluorosulfonyl fluoride and ester-substituted cyclopropanes, **1d** and **1f**, were fairly tolerant to the reaction conditions and could be prepared in greater than 80% yields from the corresponding funtionalized perfluorovinyl ethers, whereas the nitrile-substituted vinyl ether gave the corresponding cyclopropane **1e** in 44% yield. Chlorotrifluoroethylene and trifluoroethylene gave good yields of **1g** and **1h**, respectively, while bromotrifluoroethylene only produced bromopentafluorocyclopropane, **1i**, in modest to low yields. The observation of significant amounts of viscous oil indicated the bromotrifluoroethylene thermally oligomerized at 180 °C. It has been reported that bromotrifluoroethylene and difluorocarbene from $(CF_3)_3PF_2$ at 120 °C gave the cyclopropane **1i** in 61% yield.[7] Interestingly, the oligomerization could be suppressed and the yield of **1i** improved by the addition of small amounts of a radical inhibitor.



1

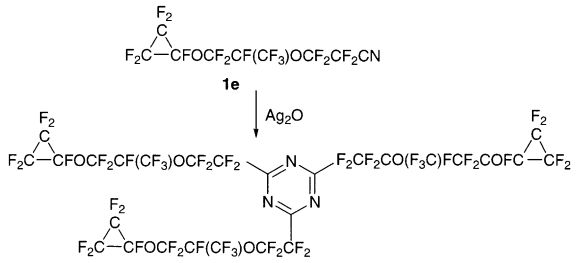
Difluorocarbene from HFPO also added to 1,1-difluorinated ethylenes under similar conditions. Reaction with 1,1-dichlorodifluoroethylene or vinylidene fluoride gave good yields of the tetrafluorinated cyclopropanes, **1j** and **1k**, respectively, but 1,1-dibromodifluoroethylene gave only low yields of tetrafluorodibromocyclopropane **1l**.

TABLE 1. Preparation of Fluorinated Cylcopropanes 1

compd no.	X	Y	yield (%)
1a	F	F	80
1b	F	OCF_3	76
1c	F	OC_3F_7	67
1d	F	$OCF_2CF(CF_3)OCF_2CF_2CO_2Me$	83
1e	F	$OCF_2CF(CF_3)OCF_2CF_2CN$	44
1f	F	$OCF_2CF(CF_3)OCF_2CF_2SO_2F$	80
1g	F	Cl	74
1h	F	H	67
1i	F	Br	63
1j	Cl	Cl	61
1k	H	H	55
1l	Br	Br	28

With a mixture of *cis*- and *trans*-1,2-difluorodichloroethylene, a mixture of *cis*- and *trans*-1,2-dichlorotetrafluorocyclopropane, **1m**, was obtained in the same ratio as starting material as reported in the literature.[6a,13b]

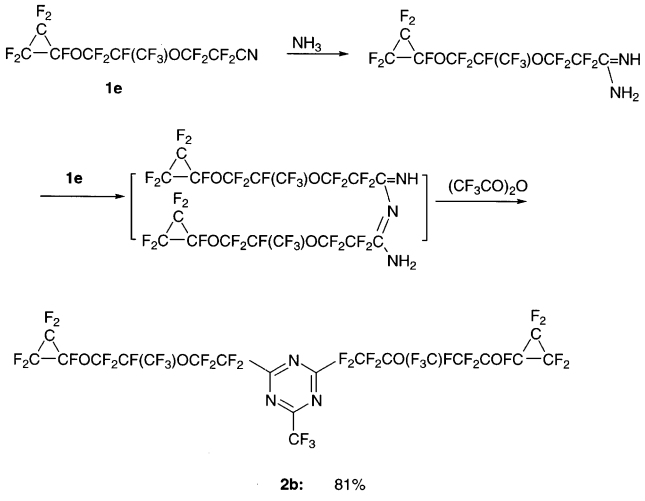
Multi(pentafluorocyclopropane) compounds **2** were prepared from **1e**. It has been well documented that fluorinated nitrile compounds can be trimerized into fluorinated s-triazines in high yields.[8] When c-$C_3F_5OCF_2$-$CF(CF_3)OCF_2CF_2CN$ was treated with catalytic amounts of Ag_2O at 120−140 °C neat for 10 h, the corresponding s-triazine **2a** was formed in 80% isolated yield.



2a

80%

Di(pentafluorocyclopropanyl)triazine (**2b**) was also prepared from **1e**. **1e** was first treated with excess NH_3 at −78 °C. After warming to room temperature over 2 h the excess NH_3 was evaporated under vacuum. The residue was diluted with ether and 1 equiv of **1e** was added. The resulting mixture was stirred for 2 h. Finally, excess trifluoroacetic anhydride was added, and the resulting mixture was refluxed overnight to give the desired di-(pentafluorocyclopropanyl)-substituted triazine **2b** in 81% overall yield.[9]



2b: 81%

II. Ring-Opening Reactions of Fluorinated Cyclopropanes with Halogens. Fluorine substituents

(6) (a) Sargeant, P. B.; Krespan, C. G. *J. Am Chem. Soc.* **1969**, *91*, 415. (b) Sargeant, P. B. *J. Org. Chem.* **1970**, *35*, 678. (c) Birchall, J. M.; Fields, R.; Haszeldine, R. N.; McLean, R. J. *J. Fluorine Chem.* **1980**, *15*, 487. (d) Chepik, S. D.; Petrov, V. A.; Galakhov, M. V.; Belen'kii, G. G.; Mysov, E. I.; German, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, *8*, 1844.

(7) Birchall, M. J.; Fields, R.; Haszeldine, R. N.; Kendall, N. T. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1773.

(8) (a) Reilly, W. L.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 698. (b) Brown, H. C.; Schuman, P. D. *J. Org. Chem.* **1963**, *28*, 112. (c), Fedorova, G. B.; Dolgopolskii, I. M. J. *Gen. Chem. USSR* **1969**, *39*, 2710. (d) Young, J. A.; Dressler, R. L. *J. Org. Chem.* **1967**, *32*, 2237.

(9) *Fluoropolymers*; Wall, L. A., Ed.; Wiley-Interscience, New York, 1971.

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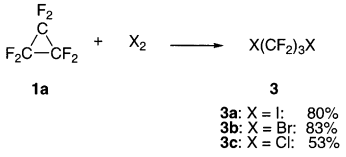
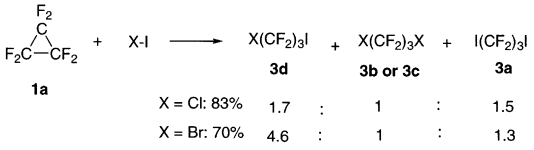
(13) (a) Haszeldine, R. N.; Rowland, R.; Speight, J. G.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1980**, 314. (b) Birchall, J. M.; Haszeldine, R. N.; Roberts, D. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1071.

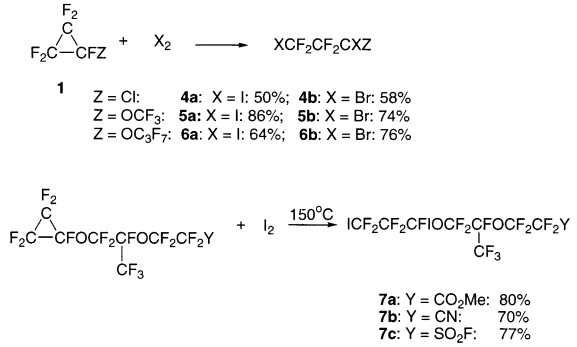
significantly affect both the structure and reactivity of cyclopropanes.[10] Hexafluorocyclopropane is much less stable thermally than its hydrocarbon counterpart,[11] and its strain energy is about twice that of cyclopropane.[10b,12] At 70−190 °C, it extrudes difluorocarbene (E_a = 38.6 kcal/mol),[11b] which can be trapped by alkenes to give difluorocyclopropane derivatives.[11,13] The CF_2: extrusion process is considered to be concerted, and in general there is no direct evidence for homolytic cleavage of carbon−carbon bonds in cyclopropanes. We discovered that highly fluorinated cyclopropanes thermally undergo ring-opening reactions with halogens to give 1,3-dihalofluoropropanes in good yields.[4b]

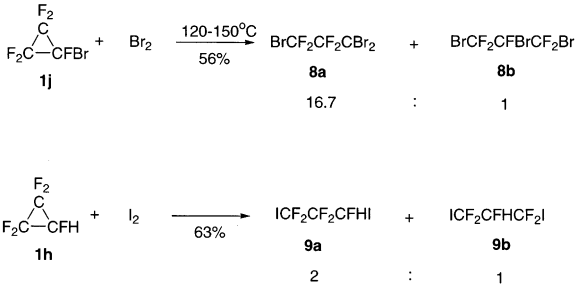


When hexafluorocyclopropane **1a** was heated with halogens at 155 °C in a Shaker tube, the corresponding 1,3-dihalohexafluoropropanes were obtained in 50−80% isolated yields. The trifluoroacetyl fluoride byproduct produced in the preparation of F-cyclopropanes from HFPO does not interfere with the ring-opening reactions with halogens, and it is therefore unnecessary to purify the fluorocyclopropane. The dihalides $X(CF_2)_3X$ can thus be prepared by first heating HFPO at 180−190 °C, adding the halogen X_2, and then heating to 150−190 °C. With iodine and bromine, **3a** and **3b** were obtained in 80% and 83% yeilds, respectively. Reaction of **1a** with chlorine gave a modest yield of **3c**, probably due to its high volatility. The ring-opening reaction can also be carried out with interhalogens such as I−X (X = Br, Cl). With I−Br and **1a** at 240 °C, a 4.6:1:1.3 mixture of $I(CF_2)_3Br$:$Br(CF_2)_3Br$:$I(CF_2)_3I$ was isolated in 70% yield. Similarly, the major product with I−Cl was $Cl(CF_2)_3I$ along with $Cl(CF_2)_3Cl$ and $I(CF_2)_3I$ (83% total yield).

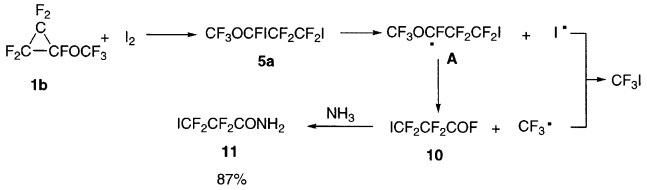


Substituted cyclopropanes readily undergo the ring-opening reactions. With pentafluorocyclopropanes bearing chlorine, bromine, and perfluoroalkoxy substituents, the ring opening occurred under milder conditions. The regiochemistry of the ring-opening reactions depends on the substituents. Chlorine- and perfluoroalkoxy-substituted pentafluorocyclopropanes reacted with Br_2 or I_2 at 150−160 °C to give only XCF_2CF_2CFXY (X = Br or I; Y = Cl or R_FO) in 58 to 80% yields, which indicates the ring opening occurred exclusively at the substituted carbons. Functional groups such as ester, sulfonyl fluoride, and nitrile did not interfere with the ring-opening reaction. The high regioselectivity can be attributed to better stabilization of these substituents than that of fluorine to the radical intermediates. However, bromine- and hydrogen-substituted pentafluorocyclopropanes have less regioselectivity. Upon reaction of bromopentafluorocyclopropane and Br_2, a 16.7:1 mixture of $BrCF_2CF_2$-$CFBr_2$:$BrCF_2CFBrCF_2Br$ resulted, whereas pentafluorocyclopropane reacted unselectively with I_2 to give a 2:1 mixture of ICF_2CF_2CFHI:ICF_2CFHCF_2I.

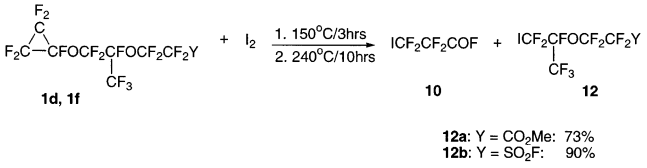




Perfluoroalkoxycyclopropanes reacted with I_2 at 240 °C to form ICF_2CF_2COF and R_FI in quantitative yields via decomposition of the primary product $R_FOCFICF_2CF_2I$. This reaction pathway is supported by the observation that authentic $R_FOCFICF_2CF_2I$ cleanly decomposed to R_FI and ICF_2CF_2COF at 240 °C. The possible mechanism of this transformation is through a radical intermediate. The iodine and carbon bond is readily cleaved to produce an intermediate **A** at high temperature due to the stabilization of the radical by an adjacent oxygen. The intermediate **A** extrudes a perfluoroalkyl radical to form the acyl fluoride **10**. After heating a mixture of **1b** with iodine at 150−180 °C for 1 h and at 240 °C for 8 h, the resulting mixture was treated with NH_3 in ether to give $ICF_2CF_2CONH_2$ in 87% overall yield.

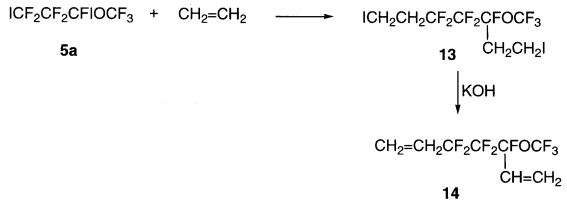


This chemistry was used to synthesize other more complex functionalized iodides, which were used to make functional materials as illustrated below.

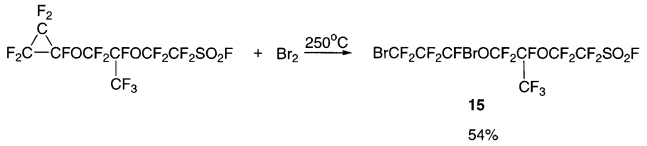


In the presence of ethylene, the perfluorodiiodoether **5a** was heated at 180 °C to give an excellent yield of the

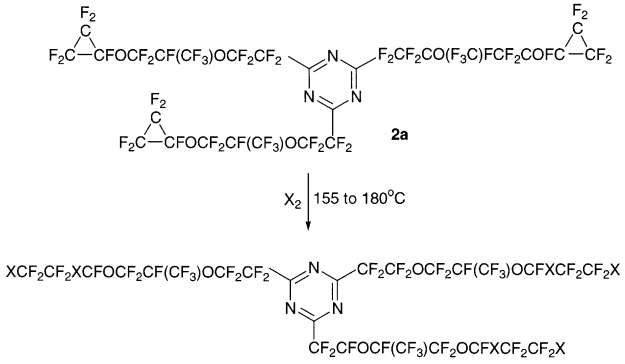
diadduct **13**, which could then be treated with KOH to form the diene **14**.



The ring-opening products from perfluoroalkoxycyclopropanes and bromine decomposed much slowly than the corresponding products from iodine, due to the stronger bromine−carbon bond than that of iodine−carbon. After a mixture of perfluoroalkoxycyclopropane and Br_2 was heated at 150 °C for 3 h and at 250 °C for 20 h, the ring-opening product was found mostly unreacted and could be isolated in 54% yield.



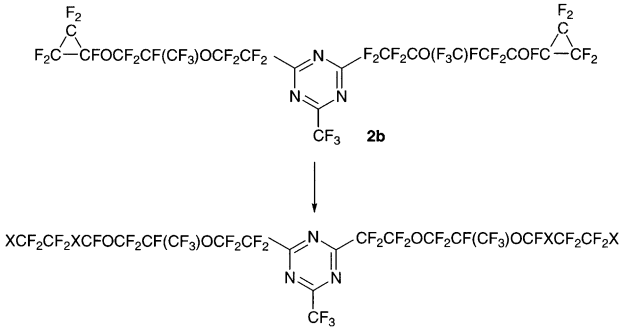
The ring-opening reaction could be extended to multi(perfluorocyclopropane) derivatives, thus yielding various materials which could not be prepared by other means. For example, when the triazine derivative **2a** was heated with halogens such as iodine and bromine at 140−200 °C, the corresponding ring-opened products were obtained in 88−96% yields. The reactions were carried out neat or in perfluorinated solvents such as 2-perfluorobutyltetrahydrofuran.



16a: X = I: 88%
16b: X = Br: 96%

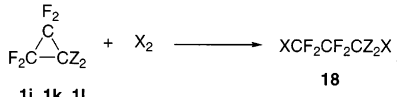
Similarly, the bis(perfluorocyclopropane) compound **2b** also reacted with halogens to give the corresponding ring-opened products in high yields.

Although tetrafluorocyclopropanes have less strain energy than hexafluorocyclopropane and substituted pentafluorocyclopropanes, they decompose to difluorocarbene when heated above 200 °C.[13] However, no ring-opening reactions have been reported. I found tetrafluorocyclopropanes also underwent ring-opening reactions with halogens at elevated temperatures. Reaction of 1,1-dichlorotetrafluorocyclopropane with bromine gave only one product $BrCF_2CF_2CCl_2Br$, whereas a mixture



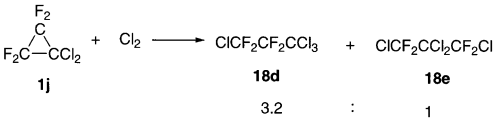
17a: X = Br: 96%
17b: X = I: 83%

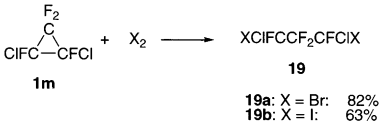
of $ClCF_2CF_2CCl_3$ and $ClCF_2CClCF_2Cl$ was obtained in a 3.2 to 1 ratio with chlorine. Similarly, upon treatment of 1,1-dibromotetrafluorocyclopropane with Br_2, ring opening occurred exclusively at the bromine-substituted carbon. Reaction of tetrafluorocyclopropane with iodine required a higher temperature to give $ICF_2CF_2CH_2I$, along with other byproducts such as $ICF_2CF_2CF_2CF_2CH_2I$, at 260 °C. With bromine, only an insoluble black solid was obtained at 260 °C.



18a: Z = Cl, X = Br: 78%
18b: Z = Br, X = Br: 95%
18c: Z = H, X = I: 35%

When 1,2-dichlorotetrafluorocyclopropane was used as a substrate, 1,3-dihalodichlorotetrafluoropropanes were formed exclusively with bromine or iodine. The regiospecificity is due to the fact that chlorine stabilizes a radical better than fluorine. In fact, thermal stereomutation of *trans*-**1m** and related compounds to their cis isomers has been reported.[6b,14] The process was proposed via the intermediacy of a trimethylene diradical. Thus, in the presence of halogens, the trimethylene diradical can be trapped to give **19**.





19a: X = Br: 82%
19b: X = I: 63%

In conclusion, I have synthesized various highly fluorinated cyclopropane derivatives in modest to high yields from the reaction of the appropriate fluoroolefins and hexafluoropropylene oxide (HFPO) at elevated temperatures. The highly fluorinated cyclopropanes have high strain and when heated with halogens or interhalogens, did not undergo the difluorocarbene extrusion

(14) (a) Ferrero, J. C.; de Staricco, E. A. R.; Staricco, E. H. *J. Phys. Chem.* **1975**, *79*, 1242. (b) Ferrero, J. C.; Staricco, E. H. *Int. J. Chem. Kinet.* **1979**, *11*, 1287. (c) Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, *99*, 4532.

reaction as described previously in the literature, but instead, ring-opening reaction occurred to give 1,3-dihalopropanes in good yields. Various functional groups in the cyclopropanes such as nitrile, sulfonyl, ester, ether, halogens, and triazine could be tolerated in the ring-opening reaction. Thus, various fluorinated 1,3-di- and polyhalides could be readily prepared which could not be readily made by other means.

Experimental Section

All fluorinated starting materials are DuPont products except CF_2=CX_2 (X = Cl, Br) and CFCl=CFCl, which were obtained from SynQuest Laboratories Inc. $CFCl_3$ is used as an internal reference in ^{19}F NMR.

General Preparation of Fluorinated Cyclopropanes 1. An autoclave was charged with the desired fluorinated olefin and 1.1 to 1.4 equiv of hexafluoropropylene oxide (HFPO) and heated at 180−190 °C for 8−10 h. After venting CF_3COF, the residue was distilled to give fluorinated cyclopropanes **1**. If the product was a gas, the reaction mixture was distilled at low temperature to give product **1**. Compounds **1a**, **1b**, **1c**, **1g**, **1h**, **1i**, **1j**, **1l**, and **1m** are known.[6,13]

Preparation of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (1d). Reaction of 425 g of CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ and 335 g of HFPO gave 391.6 g (83%) of **1d**: Bp 83−84 °C/35 mmHg. ^{19}F NMR δ −80.4 (s, 3F), −83.5 (m, 2F), −85.2 to −86.4 (m, 2F), −121.6 (s, 2F), −145.7 (t, J = 22 Hz, 1F), −152.9 9d, J = 193.4 Hz, 2F), −155.7 (dm, J = 194 Hz, 2F), −162.4 (t, J = 8.7 Hz, 1F). ^1H NMR δ 3.97 (s). IR (neat): 1791 (s), 1308 (s), 1276 (s), 1239 (s), 1152 (s) cm^{-1}. Anal. Calcd for $C_{10}H_3F_{15}O_4$: C, 25.44; H, 0.64. Found: C, 26.19; H, 0.73.

Preparation of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CN$ (1e): Bp 119−120 °C. ^{19}F NMR δ −80.3 (m, 3F), −84.6 (m, 2F), −85.7 (m, 2F), −108.7 (t, J = 5.0 Hz, 2F), −145.1 (t, J = 19 Hz, 1F), −152.8 (dm, J = 194.3 Hz, 2F), −155.5 (dm, J = 194.3 Hz, 2F), −162.4 (t, J = 9 Hz, 1F). IR (neat): 2270 (w), 1312-(s), 1278 (s), 1248 (s), 1179 (s), 1157 (s), 1121 (s) cm^{-1}. Anal. Calcd for $C_9F_{15}NO_2$: C, 24.62; F, 64.90; N, 3.19. Found: C, 25.03; F, 65.68; N, 2.93.

Preparation of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2SO_2F$ (1f): bp 91 °C/120 mmHg. ^{19}F NMR δ +45.1 (m, 1F), −80.4 (m, 3F), −85.2 (dm, J = 143.1 Hz, 1F), −85.9 (dm, J = 143 Hz, 1F), −112.4 (s, 2F), −145.2 (t, J = 21.5 Hz, 1F), −153.0 (dm, J = 201 Hz, 2F), −155.8 (dm, J = 201 Hz, 2F), −162.7 (t, J = 9 Hz, 1F). IR (neat): 1468 (s), 1278 (s), 1245 (s), 1158 (s), 1139 (s), 987 (s) cm^{-1}.

Preparation of 1,1-dibromotetrafluorocyclopropane (1k): Bp 81−82 °C. ^{19}F NMR δ −136.4 (s). HRMS calcd for $C_3F_4Br_2$ 269.8304, found 269.8257. Anal. Calcd for C_3F_4Br: C, 13.26. Found: C, 13.61.

Preparation of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CN$ (2a). A mixture of 70 g of **1e** and 0.8 g of Ag_2O was stirred at 140 °C for 20 h. The solids were removed by filtration through Celite and washed with 1,1,2-trifluorotrichloroethane (CFC113). After removal of CFC113, the filtrate was purified by chromatography on silica gel with use of a mixture of hexane and ethyl acetate in a 90 to 10 ratio as eluent to give 55.3 g of **2a**. ^{19}F NMR δ −79.9 (m, 9F), −81.4 (m, 6F), −84.9 (s, 6F), −117.9 (d, J = 13.8 Hz, 6F), −144.4 (t, J = 22.1 Hz, 3F), −152.4 (ddm, J = 198, 34 Hz, 6F), −155.3 (dm, J = 198 Hz, 6F), −162.5 (m, 3F). IR 1556 (s), 1314−1031 (vs), 985 (s), 869 (s) cm^{-1}. Anal. Calcd for $C_{29}F_{45}N_3O_6$: C, 24.62. Found: C, 24.78.

Preparation of [c-$C_3F_7OCF_2CF(CF_3)OCF_2CF_2]_2C_3N_3CF_3$ (2b). To a stirred solution of 9.0 g of **1e** and 20 mL of ether was added excess NH_3 at −40 °C. The resulting mixture was stirred at −40 to −30 °C for 2 h and then warmed to 0 °C. After removal of all volatiles at room temperature in a vacuum, the residue was diluted with 10 mL of ether and an additional 8.6 g of **1e** was added at −40 °C. The mixture was stirred at room temperature overnight and then 20.0 g of $(CF_3CO)_2O$ was added at 0 °C. The resulting reaction mixture was stirred at room temperature for 2 h and at 40 °C overnight. After evaporation of volatiles, the residue was distilled to give 15.7 g of **2b**. Bp 88−89 °C/0.6 mmHg. ^{19}F NMR δ −72.6 (s, 3F), −80.3 (m, 6F), −82.2 (m, 4F), −85.6 (m, 4F), −118.6 (s, 4F), −145.2 (t, J = 21.7 Hz, 2F), −153.0 (ddm, J = 196.8, 48.6 Hz, 4F), −155.7 (dm, J = 196.1 Hz, 4F), −162.7 (t, J = 8.8 Hz, 2F). Anal. Calcd for $C_{20}F_{33}N_3O_4$: C, 24.68; N, 4.32. Found: C, 24.87; N, 4.83.

Preparation of 1,3-Diiodohexafluoropropane (3a). A shaker tube was charged with 38 g of iodine and 30 g of hexafluorocyclopropane and heated at 155 °C for 20 h. After the tube was cooled to room temperature, 56.4 g of liquid was washed with aqueous Na_2SO_3 and brine. Distillation gave 48.3 g (80%) of product. Bp 75.5 °C/150 mmHg. ^{19}F NMR δ −58.1 (t, J = 5.0 Hz, 4F), −105.2 (t, J = 5.0 Hz, 2F). Anal. Calcd for $C_3F_6I_2$: C, 8.92; F, 28.23; I, 62.85. Found: C, 9.13; F, 28.12; I, 61.45.

Preparation of 1,3-dibromohexafluoropropane (3b): Bp 72−74 °C. ^{19}F NMR δ −63.0 (s, 4F), −113.4 (s, 2F). Anal. Calcd for $C_3F_6Br_2$: C, 11.63; Br, 51.58. Found: C, 11.62; Br, 52.12.

Preparation of 1,3-dichlorohexafluoropropane (3c): Bp 35−36 °C. ^{19}F NMR δ −67.7 (s, 4F), −119.2 (s, 2F). Anal. Calcd for $C_3F_6Cl_2$: F, 51.60. Found: F, 51.91.

Reaction of Hexafluorocyclopropane (1a) with Bromine Monoiodide. A shaker tube was charged with 52 g (0.251 mol) of BrI and 40.0 g (0.25 mol) of **1a** and heated at 240 °C for 20 h. After the tube was cooled to room temperature, 69.3 g of crude products was obtained. ^{19}F NMR analysis indicated a mixture of **3b** and **3d** (X = Br) and **3a** in a ratio of 1:4.6:1.3 (mol). Distillation gave 22.3 g of a mixture of **3b** and **3d** (X = Br), bp 73−102 °C, 12.0 g of pure **3d** (X = Br), bp 103−104 °C, 17.0 g of a mixture of **3d** (X = Br) and **3a**, bp 108−103 °C, and 8.4 g of pure **3a**, bp 132 °C. ^{19}F NMR for **3d** (X = Br) δ −58.6 (m, 2F), −61.3 (m, 2F), −109.3 (m, 2F). Anal. Calcd for C_3F_6BrI: C, 10.10; F, 31.95; Br, 22.39; I, 35.56. Found: C, 1045; F, 31.77; Br, 21.72; I, 36.90.

Reaction of Hexafluorocyclopropane (1a) with Chlorine Monoiodide. A shaker tube was charged with 16.3 g (0.1 mol) of ICl and 20.0 g (0.125 mol) of **1a** and heated at 230 °C for 10 h. After the tube was cooled to room temperature, 29.2 g of crude products was obtained. ^{19}F NMR analysis indicated three main products, **3c** and **3d** (X = Cl) and **3a** in a ratio of 1:1.75:1.5 (mol). Distillation gave 3.9 g of **3c**, bp 34−35 °C, 3.4 g of a mixture of **3c** and **3d** (X = Cl), bp 40−79 °C, 3.0 g of pure **3d**, bp 80−81 °C, 5.5 g of a mixture of **3d** (X = Cl) and **3a**, bp 83−133 °C, and 9.8 g of pure **3a**, bp 133−135 °C. ^{19}F NMR for **3d** (X = Cl) δ 58.8 (tt, J = 13.1, 5.0 Hz, 2F), −66.9 (t, J = 13.1 Hz, 2F), −112.1 (s, 2F).

Preparation 1,3-diiodo-1-chloroperfluoropropane (4a): Bp 86−88 °C/50 mmHg. ^{19}F NMR δ −51.7 (ddd, J = 201.9, 9.0, 6.6 Hz, 1F), −55.8 (ddd, J = 201.7, 24.8, 7.0 Hz, 1F), −72.8 (m, 1F), −94.6 (ddd, J = 268.3, 13.7, 7.0 Hz, 1F), −102.9 (ddd, J = 268.3, 15.3, 9.2 Hz, 1F). Anal. Calcd for $C_3F_5ClI_2$: C, 8.57; F, 22.60; Cl, 8.44; I, 60.39. Found: C, 8.52; F, 22.53; Cl, 7.52; I, 62.27.

Preparation 1,3-dibromo-1-chloroperfluoropropane (4b): Bp 114−115 °C. ^{19}F NMR δ −58.5 (ddt, J = 178.1, 10.8, 4.6 Hz, 1F), −60.0 (ddm, J = 178, 16.6 Hz, 1F), −70.8 (m, 1F), −106.7 (dm, J = 268.7 Hz, 1F), −109.4 (dm, J = 268.1 Hz, 1F). Anal. Calcd for $C_3F_5ClBr_2$: C, 11.04; F, 29.11; halogen calcd as Cl, 32.59. Found: C, 10.53; F, 29.33; halogen calcd as Cl, 32.24.

Preparation of 1,3-diiodopentafluoropropyl trifluoromethyl ether (5a): Bp 80−81 °C/100 mmHg. ^{19}F NMR δ −54.9 (d, J = 10.7 Hz, 3F), −60.8 (ddm, J = 180.4, 5.5 Hz, 1F), −62.8 (ddm, J = 180.4, 21.1 Hz, 1F), −71.1 (m, 1F), −111.8 (dd, J = 274.2, 5.4 Hz, 1F), −112.9 (ddd, J = 275, 7.5, 4.3 Hz, 1F). Anal. Calcd for $C_4F_8I_2O$: C, 10.23; F, 32.35; I, 54.02. Found: C, 10.99; F, 32.01; I, 53.73.

Preparation of 1,3-dibromopentafluoropropyl trifluoromethyl ether (5b): Bp 99 °C. ^{19}F NMR δ −54.9 (d, J = 10.7 Hz, 3F), −60.8 (ddm, J = 180.4, 5.5 Hz, 1F), −62.8 (ddm, J = 180.4, 21.1 Hz, 1F), −71.1 (m, 1F), −111.8 (dd, J = 274.2, 5.4 Hz, 1F), −112.9 (ddd, J = 275, 7.5, 4.3 Hz, 1F). Anal. Calcd for $C_4F_8Br_2O$: C, 12.78; F, 40.44; Br, 42.52. Found: C, 12.72; F, 42.67; Br, 42.73.

Preparation of 1,3-diiodopentafluoropropyl heptafluoropropyl ether (6a): Bp 85−86 °C/40 mmHg. ^{19}F NMR δ −55.3 (d, J = 204.6 Hz, 1F), − 58.8 (ddd, J = 204.6, 27, 6.3 Hz, 1F), −68.7 (m, 1F), −81.3 to −81.9 (m, 4F), −90.7 (d, J = 147.6 Hz, 1F), −102.4 (dt, J = 276.7, 8 Hz, 1F), −104.4 (dt, J = 276.6, 7.5 Hz, 1F), −130.4 (s, 2F). Anal. Calcd for $C_6F_{12}I_2O$: C, 12.65; F, 40.01; I, 44.54. Found: C, 12.57; F, 40.29; I, 45.06.

Preparation of 1,3-dibromopentafluoropropyl heptafluoropropyl ether (6b). Bp 134 to 135 °C. ^{19}F NMR δ −61.0 (dt, J = 180.3, 4.3 Hz, 1F), −63.1 (dd, J = 180.8, 22.6 Hz, 1F), −71.0 (m, 1F), −81.6 (m, 3F), −83.2 (dm, J = 146.5 Hz, 1F), −87.5 (dt, J = 146.5, 7.6 Hz, 1F), −112.3 (m, 2F), −130.3 (m, 2F). Anal. Calcd for $C_6F_{12}Br_2O$: C, 15.14; F, 47.91; Br, 33.58. Found: C, 14.78; F, 47.75; Br, 32.30.

Reaction of c-$C_3F_7OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (1d) with Iodine. 7a: Bp 107−110 °C/3 mmHg, ^{19}F NMR δ −55.2 (d, J = 205.1 Hz, 1F), −58.8 (dm, J = 204.4 Hz, 1F), −69.0 (m, 1F), −80.0 (s, 3F), −79.6 to −80.7 (m, 1F), −82.5 to −84.0 (m, 2F), −89.9 (m, 0.5 F), −90.3 (m, 0.5F), −102.1 (d, J = 277.1 Hz, 1F), −104.6 (dt, J = 277, 8.4 Hz, 1F), −121.5 (s, 2F), −145.7 (t, J = 11.3 Hz, 0.5F), −146.0 (t, J = 11.7 Hz, 0.5F). ^{1}H NMR δ 4.01 (s). IR (neat): 1786 (s), 1243 (s), 1194 (s), 1152 (s) cm^{-1}. Anal. Calcd for $C_{10}H_3F_{15}I_2O_4$: C, 16.55; H, 0.42; I, 34.96. Found: C, 17.03; H, 0.51; I, 35.21.

Reaction of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CN$ (1e) with Iodine. 7b: Bp 77 °C/5 mmHg. ^{19}F NMR δ −55.4 (d, J = 205.1 Hz, 1F), −58.8 (ddd, J = 205.5, 27.3, 5.2 Hz, 1F), −69.4 (m, 1F), −79.1 to −80.4 (m, 4F), −84.1 to −85.2 (m, 2F), −89.9 (dm, J = 152.5 Hz, 1F), 102.0 (dm, J = 277.9 Hz, 1F), −104.5 (dm, J = 278.4 Hz, 1F), −108.6 (s, 2F), −145.1 (t, J = 21.2 Hz, 0.5F), −145.6 (t, J = 21.3 Hz, 0.5F). IR (neat): 2269 (w), 1245 (s), 1180 (s) cm^{-1}. Anal. Calcd for $C_9F_{15}I_2NO_2$: C, 15.60; I, 36.63; N, 2.02. Found: C, 15.63; I, 37.50; N, 2.14.

Reaction of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2SO_2F$ (1f) with Iodine. 7c: Bp 97 °C/4.8 mmHg. ^{19}F NMR δ +45.3 (m, 1F), −55.6 (d, J = 204.7 Hz, 1F), −58.9 (ddd, J = 204.7, 27.2, 6.3 Hz, 1F), −69.3 (m, 1F), −79.3 to −80.2 (m, 6F), −89.8 (dm, J = 144.3 Hz, 1F), −101.9 (dm, J = 277.9 Hz, 1F), −104.6 (dt, J = 277.8, 7.7 Hz, 1F), −112.2 (m, 2F), −145.4 (m, 1F). IR (neat): 1465 (s), 1245 (vs), 1198 (s) cm^{-1}. Anal. Calcd for $C_8F_{16}SO_4I_2$: C, 12.81; F, 40.53; I, 33.84; S, 4.28.

Reaction of Bromopentafluorocyclopropane (1j) with Bromine. 8a and **8b**: Bp 92−93 °C/200 mmHg. ^{19}F NMR for **8a** δ −58.3 (d, J = 15.2 Hz, 2F), −72.3 (tt, J = 15.2, 13.7 Hz, 1F), −106.2 (d, J = 13.7 Hz, 2F). ^{19}F NMR for **8b** δ − 54.7 (dm, J = 178 Hz, 2F), −56.3 (dm, J = 178.1 Hz, 2F), −123.4 (pent, J = 15 Hz, 1F). Anal. Calcd for $C_3F_5Br_3$: C, 9.72; F, 25.62. Found: C, 10.21; F, 24.95.

Reaction of Pentafluorocyclopropane (1h) with Iodine. A shaker tube was charged with 25.4 g of I_2 and 14 g of pentafluorocyclopropane and heated at 190 °C for 3 h and 210 °C for 2 h. After the tube was cooled to room temperature, the crude product was washed with aqueous Na_2SO_3 to give 24.3 g of material. ^{19}F NMR and ^{1}H NMR analysis indicated a mixture of ICF_2CF_2CFHI (**9a**) and ICF_2CFHCF_2I (**9b**) in a 2:1 ratio. ^{1}H NMR for ICF_2CF_2CFHI δ 7.16 (ddd, J = 47.6, 20.7, 1.5 Hz). ^{1}H NMR for ICF_2CFHCF_2I δ 4.80 (dtt, J = 42.1, 14.8, 3.3 Hz, 1H). ^{19}F NMR for ICF_2CF_2CFHI δ −52.6 (dm, J = 207.8 Hz, 1F), −54.8 (dm, J = 207.8 Hz, 1F), −101.0 (ddt, J = 273.1, 32.3, 6.3 Hz, 1F), −116.3 (dm, J = 273.1 Hz, 1F), 165.7 (m, 1F). ^{19}F NMR for ICF_2CFHCF_2I δ −57.9 (dm, J = 207.8 Hz, 2F), −59.8 (dt, J = 207.8, 6.5 Hz, 2F), −176.2 (m, 1F). HRMS calcd for $C_3HCF_5I_2$ 385.8088, found 385.7962 for ICF_2CF_2CFHI and 385.8171 for ICF_2CFHCF_2I. Anal. Calcd for $C_3F_5HI_2$: C, 9.34; H, 0.26; F, 24.62. Found: C, 9.00; H, 0.22; F, 24.81.

Preparation of 3-Iodotetrafluoropropionyl Amide (11). An autoclave was charged with 254 g of iodine and 220 g of trifluoromethoxypentafluorocyclopropane and heated at 150−180 °C for 1 h and 240 °C for 8 h. After the tube was cooled to room temperature and gas was vented, 426.8 g of crude product **10** was obtained, which was dissolved in 800 mL of ether, then NH_3 has was added at −78 °C to room temperature until the solution was basic. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with water and dried over $MgSO_4$. After removal of the ether, the residue was re-crystallized from a mixture of hexane and ether to give 244.6 g (87%) of $ICF_2CF_2CO_2NH_2$, **11**: Mp 136−137 °C. ^{19}F NMR δ −62.3 (t, J = 5 Hz, 2F), −112.1 (t, J = 5 Hz, 2F). ^{1}H NMR δ 7.99 (br, 1H), 7.69 (br, 1H). Anal. Calcd for $C_3H_2F_4NOI$: C, 13.30; H, 0.74; F, 28.05; I, 46.84. Found: C, 13.35; H, 0.78; F, 27.10; I, 46.87.

Reaction of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ (1d) with Iodine at 240 °C. A 0.4-L shaker tube was charged with 189 g of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$ and 100 g of I_2 and heated at 150 °C for 3 h and 240 °C for 8 h. Distillation of the reaction mixture gave 78.3 g of ICF_2CF_2COF (**10**), bp 57−58 °C, and 129.3 g of $ICF_2CF(CF_3)OCF_2CF_2CO_2Me$ (**12a**), bp 98−100 °C/60 mmHg. ^{19}F NMR for **10** δ +28.0 (m, 1F), −62.1 (m, 2F), −111.4 (m, 2F). ^{19}F NMR for **12a** δ −58.8 (dm, J = 210 Hz, 1F), −59.9 (dm, J = 210 Hz, 1F), −76.8 (m, 3F), −82.7 (dm, J = 158.7 Hz, 1F), −83.7 (dm, J = 158 Hz, 1F), −121.6 (t, J = 3.3 Hz, 2F), −134.3 (m, 1F). IR for ICF_2CF_2COF 1768 (s), 1187 (s), 1150 (s) cm^{-1}. IR for $ICF_2CF(CF_3)CF_2CF_2CO_2Me$ 1768 (s), 1342 9s), 1304 (s), 1232 to 1110 (s) cm^{-1}. Anal. Calcd for $C_7H_3F_{10}IO_3$: C, 18.60; H, 0.67; F, 42.03. Found: C, 18.24; H, 0.52; F, 42.38.

Reaction of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2SO_2F$ (1f) with Iodine at 240 °C. A shaker tube was charged with 56 g of c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2SO_2F$ and 25 g of I_2 and heated at 150 °C for 3 h and at 240 °C for 10 h. Distillation of the reaction mixture gave 17.4 g of **10**, bp 58−59 °C, and 44.3 g of **12b**, bp100−104 °C/200 mmHg. ^{19}F NMR for $ICF_2CF(CF_3)OCF_2CF_2SO_2F$ δ +45.5 (m, 1F), −58.7 (dm, J = 213.7 Hz, 2F), −60.0 (dm, J = 214 Hz, 2F), −76.9 (m, 3F), −77.9 (dd, J = 139.2, 22.7 Hz, 1F), −79.7 (dm, J = 139.2 Hz, 1F), −122.2 (s, 2F), −133.6 (m, 1F). Anal. Calcd for $C_5F_{11}ISO_3$: C, 12.62; I, 26.66. Found: C, 12.68; I, 26.67.

Reaction of 1,3-Diiodopentafluoropropyl Trifluoromethyl Ether with Ethylene. A mixture of 50 g of $ICF_2CF_2CFIOCF_3$ and 11.0 g of CH_2=CH_2 was heated at 180 °C for 4 h and then distilled to give 55.6 g of **13**. ^{19}F NMR δ −53.2 (d, J = 12.3 Hz, 3F), −114.3 (m, 2F), −123.0 (s, 3F), −126.3 (m, 2F). ^{1}H NMR δ 3.20−3.64 (m, 4H), 2.61−2.87 (m, 4H). Anal. Calcd for $C_8H_8F_8I_2O$: C, 18.27; H, 1.53; F, 28.90; I, 48.26. Found: C, 18.59; H, 1.47; F, 29.25; I, 48.29.

Preparation of CH_2=$CHCF_2CF_2CF(OCF_3)CH$=CH_2 (14). To a stirred solution of 21.0 g of **13** and 20 mL of EtOH was added 6.7 g of KOH in 6 mL of water and 20 mL of EtOH at 75 °C. The resulting mixture was stirred for 2 h, and water was added. The lower layer was separated and washed with water and brine to give 8.3 g of 98.5% pure **14**. Distillation gave pure **14**: Bp 117−119 °C. ^{19}F NMR δ −53.4 (d, J = 17 Hz, 3F), −112.7 (m, 2F), −125.2 (s, 2F), −129.1 (t, J = 7.7 Hz, 1F). ^{1}H NMR δ 5.7 to 6.10 (m). Anal. Calcd for $C_8H_6F_8O$: C, 35.57; H, 2.24; F, 56.27. Found: C, 36.87; H, 2.23; F, 56.09.

Reaction of [c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2]_3C_3N_3$ (2a) with Bromine. A mixture of 3.94 g of **2a**, 2.1 g of Br_2, and 1.5 mL of 2-perfluorobutyltetrahydrofuran was stirred in a sealed tube at 160−170°C for 6 h. After removal of volatiles, the crude product was purified by chromatography on silica gel (hexane/ethyl acetate 90:10) to give 5.2 g (96%) of **16b**: ^{19}F NMR δ −61.3 (d, J = 181.1 Hz, 3F), −63.5 (dm, J = 181 Hz, 3F), −71.5 (m, 3F), −80.4 (s, 9F), −82.0 (m, 3F), −82.4 (s, 6F), −86.9 (m, 3F), −112.4 (m, J = 277.8 Hz, 3F), −119.0 (m, 6F), 145.6 (m, 3F). Anal. Calcd for $C_{27}F_{45}Br_6N_3O_6$: C, 18.05; N, 2.34; Br, 26.68. Found: C, 18.27; N, 2.35; Br, 25.35.

Reaction of [c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2]_3C_3N_3$ with

Iodine. 16a: ^{19}F NMR δ −55.3 (d, J = 205.2 Hz, 3F), −59.0 (dm, J = 205 Hz, 3F), −69.1 (m, 3F), −79.6 to 80.6 (m, 12F), −82.2 (m, 6F), −89.7 (m, 3F), −101.9 (dm, J = 277.8 Hz, 3F), −104.6 (dm, J = 277.8 Hz, 3F), −118.7 (m, 6F), 145.5 (m, 3F). Anal. Calcd for $C_{27}F_{45}I_6N_3O_6$: F, 41.13; N, 2.02; I, 36.62. Found: F, 41.65; N, 2.11; I, 35.27.

Reaction of [c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2]_2C_3N_3CF_3$ (2b) with Bromine. 17a: ^{19}F NMR δ −61.3 (d, J = 180.8 Hz, 2F), −63.5 (dt, J = 181.0, 10.7 Hz, 2F), −71.3 (m, 2F), −72.1 (s, 3F), −80.2 (s, 6F), −81.7 to −82.5 (m, 6F), −86.6 (m, 2F), −112.4 (m, 4F), −118.9 (m, 4F), −145.6 (m, 2F). Anal. Calcd for $C_{20}F_{33}N_3O_4Br_4$: C, 18.58; N, 3.25; Br, 24.72. Found: C, 18.51; N, 3.24; Br, 24.17.

Reaction of [c-$C_3F_5OCF_2CF(CF_3)OCF_2CF_2]_2C_3N_3CF_3$ (2b) with Iodine. 17b: ^{19}F NMR δ −55.6 (d, J = 205.1 Hz, 2F), −59.2 (dm, J = 205.7 Hz, 2F), −69.0 (m, 2F), −72.1 (s, 3F), −80.2 to −80.7 (m, 8F), −82.5 (m, 4F), −89.7 (m, 2F), −102.0 (dm, J = 277.8 Hz, 2F), −104.7 (dm, J = 278 Hz, 2F), −118.8 (m, 4F), −145.8 (m, 2F). Anal. Calcd for $C_{20}F_{33}N_3O_4I_4$: C, 16.22; N, 2.84. Found: C, 17.02; N, 2.96.

Reaction of 1,1-Dichlorotetrafluorocyclopropane (1j) with Bromine. A mixture of 5.5.0 g of 1,1-dichlorotetrafluorocyclopropane and 4.8 g of Br_2 was heated in a sealed tube at 160 °C for 2 h and at 180 °C for 4 h. Distillation of the crude product gave 8.0 g of $BrCF_2CF_2CCl_2Br$ (**18a**), bp 153−154 °C. ^{19}F NMR δ −55.5 (s, 2F), −102.0 (s, 2F). Anal. Calcd for $C_3F_4Cl_2Br_2$: C, 10.51; F, 22.17; halogen calcd as Cl, 41.37. Found: C, 10.68; F, 22.20; halogen calcd as Cl, 42.03.

Reaction of 1,1-Dibromotetrafluorocyclopropane (1l) with Bromine. A mixture of 2.72 g of 1,1-dibromotetrafluorocyclopropane and 2.0 g of Br_2 was heated in a sealed tube at 170 °C for 5 h. The crude product was washed with aqueous Na_2SO_3 solution and distilled to give 4.1 g of $BrCF_2CF_2CBr_3$ (**18b**), bp 120−122 °C/80 mmHg. ^{19}F NMR δ −53.4 (s, 2F), −98.0 (s, 2F). HRMS calcd for $C_3F_4Br_4$ 427.6672, found 427.6706. Anal. Calcd for $C_3F_4Br_4$: C,8.35. Found: C, 8.80.

Reaction of 1,1-Dihydrotetrafluorocyclopropane (1k) with Iodine. A mixture of 30 g of 1,1-dihydrotetrafluorocyclopropane and 25.4 g of I_2 was heated in a sealed tube at 270 °C for 2.5 h. The reaction mixture was washed with aqueous Na_2SO_3 to give 45.5 g of crude product, which was distilled to give 5.6 g of **18a**, bp 56−82 °C/10 mmHg, 5.8 g of **18b**, bp 82−97 °C/100 mmHg, and 10.7 g of $ICF_2CF_2CH_2I$ (**18c**), bp 97−102 °C/10 mmHg. ^{19}F NMR δ −59.5 (t, J = 4.0 Hz, 2F), −101.5 (tt, J = 16.7, 4.0 Hz, 2F). HRMS calcd for $C_3H_2F_4I_2$ 367.8182, found 367.8142. One of the byproducts is $ICF_2CF_2CF_2CF_2CH_2I$ with calcd $C_5H_2F_8I$ − I 340.9075, found 340.9076.

Reaction of 1,1-Dichlorotetrafluorocyclopropane (1j) with Chlorine. After a mixture of 11.0 g of 1,1-dichlorotetrafluorocyclopropane and 7.0 g of Cl_2 was heated in a shaker tube at 260 °C for 10 h, 11.0 g of crude product was obtained, which was distilled to give 7.1 g of product, bp 103−107 °C. ^{19}F NMR indicated a mixture of $ClCF_2CF_2CCl_3$, **18d,** and $ClCF_2CCl_2CF_2Cl$, **18e**, in a 3.2 to 1 ratio. ^{19}F NMR for $ClCF_2CF_2CCl_3$ δ −61.3 (s, 2F), −108.0 (s, 2F). ^{19}F NMR for $ClCF_2CCl_2CF_2Cl$ δ −65.1 (s). HRMS calcd for $C_3F_4Cl_4$ − Cl 216.9002, found 216.9032 for $ClCF_2CF_2CCl_3$ − Cl and 216.8995 for $ClCF_2CCl_2CF_2Cl$ − Cl.

Reaction of 1,2-Dichlorotetrafluorocyclopropane (1m) with Bromine. A mixture of 5.5 g of 1,2-dichlorotetrafluorocyclopropane and 5.3 g of Br_2 was heated in a sealed tube at 140 °C for 1 h, at 160 °C for 2 h, and at 165 °C for 1 h. After being washed with aqueous Na_2SO_3, the organic layer was distilled to give 8.4 g of $BrCFClCF_2CFClBr$ (**19a**), bp89−92 °C/100 mmHg. ^{19}F NMR indicated two diastereoisomers: first isomer δ −65.1 (t, J = 9 Hz, 2F), −102.7 (t, J = 9 Hz, 2F); second isomer δ −65.7 (t, J = 9 Hz, 2F), −108.8 (dt, J = 259, 10 Hz, 1F), −105.1 (dt, J = 259, 9.3 Hz, 1F). HRMS calcd for $C_3F_4Cl_2Br_2$ − Br 260.8497, found 260.8568.

Reaction of 1,2-Dichlorotetrafluorocyclopropane (1m) with Iodine. A mixture of 5.5 g of 1,2-dichlorotetrafluorocyclopropane and 8.9 g of I_2 was heated in a sealed tube at 140 °C for 1 h, at 160 °C for 2 h, and at 165 °C for 1 h. After being cooled to room temperature, the reaction mixture was washed with aqueous Na_2SO_3. After removal of $CF_2ClCFCl_2$, the residue (9.6 g) was distilled to give 8.3 g of $ICFClCF_2CFClI$ (**19b**), bp 120 °C/40 mmHg. ^{19}F NMR indicated two diastereoisomers: first isomer δ −65.3 (t, J = 14.6 Hz, 2F), − 91.6 (t, J = 15 Hz, 2F); second isomer δ −67.6 (t, J = 14 Hz, 2F), −88.0 (dt, J = 257, 13 Hz, 1F), −100.6 (dt, J = 257, 13 Hz, 1F). HRMS calcd for $C_3F_4Cl_2I_2$ 435.7403, found 435.7402.

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