

The reaction of CF₃OOCF₂OF with fluoroolefins

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Abstract

The reaction of fluoroxydifluoromethyl trifluoromethyl peroxide, CF₃OOCF₂OF (**1**), with fluoroolefins leads to the formation of novel fluorinated peroxides as major products. When **1** was added to 1,2-dichloro-1,2-difluoroethylene, CFCl=CFCl, under controlled conditions, the formation of 4,5-dichloro-2,2,4,5-tetrafluoro-1,3-dioxolane was also observed. A mechanism is proposed to rationalize these results.

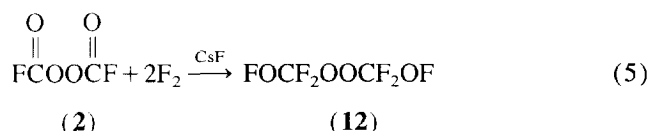
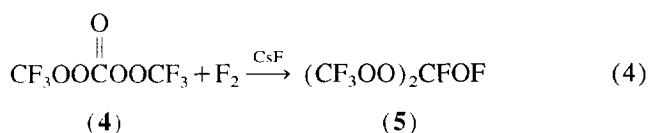
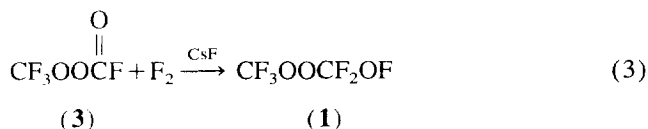
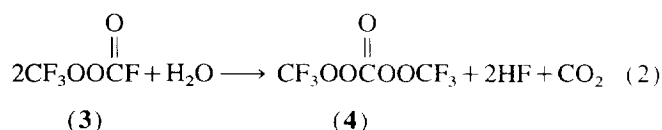
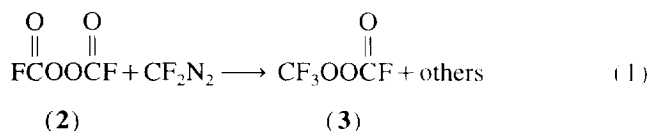
Keywords: Fluoroolefins; Fluoroxydifluoromethyl trifluoromethyl peroxide; Synthesis; IR spectroscopy; NMR spectroscopy; Mass spectrometry

1. Introduction

The reactions of perfluoroalkyl hypohalites with olefins have been exhaustively studied, and found to produce ethers by addition through the double bond. In this reaction, oligomers and polymers may be formed in variable amounts [1,2].

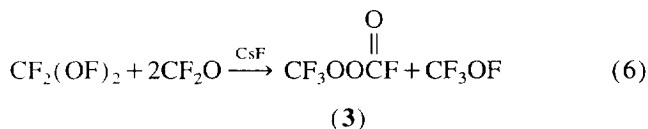
Among the perfluorocarbon compounds containing the peroxidic linkage, trioxides were added thermally to olefins producing peroxy-ethers [3], while peroxides are quite unreactive under the same conditions.

Trifluoromethyl peroxy hypofluorite, CF₃OOF, and the similar hypochlorite, CF₃OOCl, in their reactions with olefins gave peroxides [4] where the CF₃OO moiety was retained in the final products. Three compounds are known to contain the peroxy and the hypofluorite functional groups in geminal positions: CF₃OOCF₂OF (**1**), (CF₃OO)₂CFOF (**5**) and FOCF₂OOCF₂OF (**12**). They were first prepared [5,6] by the following reactions:



While the hypofluorites can be formed quantitatively [5,6], the preparation of their precursor is difficult.

A practical route to **3** [7] starts from bis(fluoroxy)difluoromethane, CF₂(OF)₂ [Eq. (6)]:



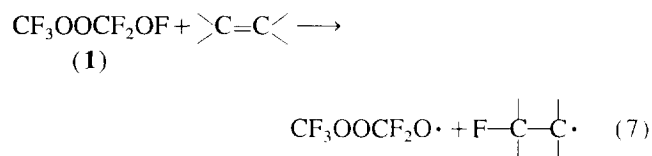
This synthesis leads to the formation of **3** in 80% yield. Thus the pure peroxy hypofluorite **1** is almost as readily available and comparatively safe to handle as CF₃OF and CF₂(OF)₂, sharing with the latter the contrast between a very remarkable stability and a disquieting structure. However the reaction of **1** with olefins has not been reported. We have studied it with regard to the behaviour of a peroxide bond under the condi-

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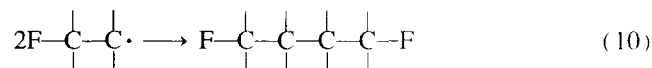
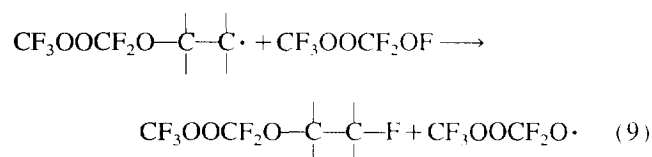
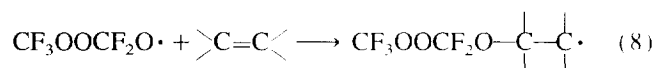
tions of a radical reaction initiated by the hypofluorite function in the same molecule.

2. Results and discussion

The major products of the reaction of **1** with fluoroolefins are those resulting from simple addition of the O—F function to the double bond, while the peroxide bond is retained. It was possible to carry out the reactions without solvent which facilitated the isolation of the products. The use of a three- to four-fold excess of the olefins improved the yields. According to a free-radical mechanism, the addition of hypofluorites to electron-poor olefins is initiated by the homolytic cleavage of the O—F bond induced by the alkene [Eq. (7)]:

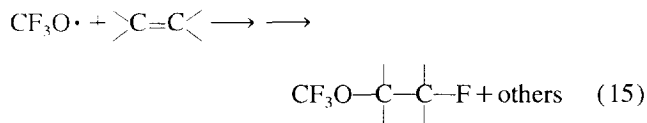
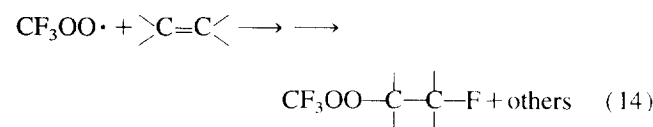
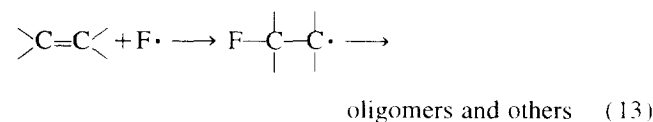
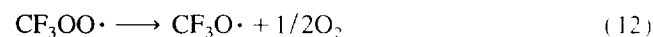
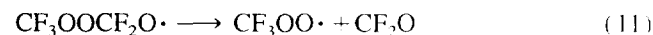


Propagation [Eqs. (8) and (9)] and termination [Eq. (10)] steps are the following:



One of the possible termination steps [Eq. (10)] is supported by the presence of typical radical-coupling products detected in traces by GLC/mass-spectroscopy.

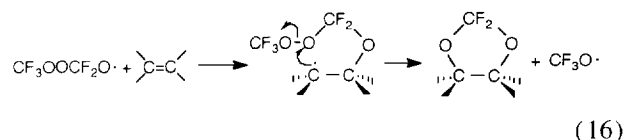
Byproducts such as COF_2 , O_2 , oligomers and compounds deriving from the addition of oxy and peroxy radicals observed in the reaction mixture can be formed through the following pathways:



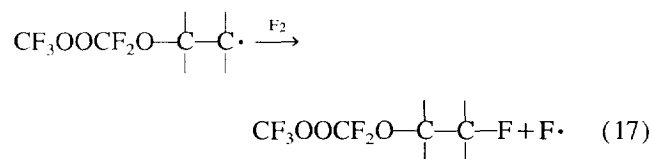
The experimental results of the present work show that the radical species $\text{CF}_3\text{OOCF}_2\text{O}\cdot$ is sufficiently long lived to account for the major products deriving from its addition to the olefinic substrate [Eq. (8)]. Moreover, the peroxy and oxy radicals of Eqs. (11) and (12) add to the olefins faster than they decompose considering the presence of their addition products [Eqs. (14) and (15)], and because oxygen and COF_2 were detected only in traces.

An interesting result was obtained when the hypofluorite **1** was added to 1,2-dichloro-1,2-difluoroethylene, $\text{ClFC}=\text{CFCl}$, at -60°C (see Experimental details below). Under these conditions, of the reaction products 4,5-dichloro-2,2,4,5-tetrafluoro-1,3-dioxolane [8–10] was formed in 25% yield, while the simple addition product, $\text{CF}_3\text{OOCF}_2\text{OCFCl}-\text{CF}_2\text{Cl}$, was formed in 27% yield. When the reaction was carried out at -100°C or in the presence of a small amount of F_2 (< 10%), the dioxolane was formed in a yield lower than 7%.

For the formation of dioxolane, in view of the known reactivity of $\text{CF}_2(\text{OF})_2$ [10], we propose the following intramolecular radical reaction:

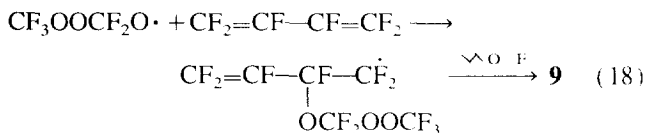


The oxy radicals generated by this reaction added to the olefins as previously suggested in Eq. (15). The chemical pathway proposed in Eq. (16) could be favourable at low concentrations of hypofluorite when it is added to the olefins. Under these conditions, the mechanism proposed in Eq. (16) becomes competitive with that reported in Eq. (9). This hypothesis is reinforced by the fact that, when a small amount of fluorine was present, only traces of dioxolane were formed. The results can be explained by the reaction between the radical intermediate and fluorine [Eq. (17)]:

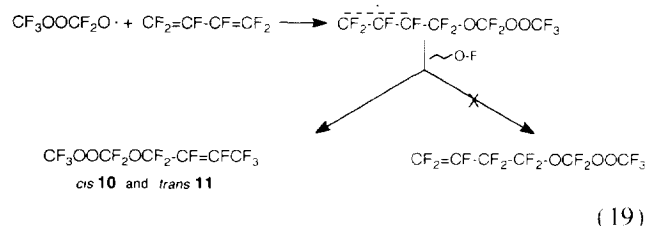


The different ratio of products obtained at temperatures lower than -60°C could be due both to thermodynamic factors and to a higher concentration of hypofluorite in solution, which favour the formation of the linear product [Eq. (9)]. No dioxolane was formed when the reaction was carried out batchwise, where the concentration of hypofluorite was higher than in the semicontinuous mode.

When **1** was added to perfluoro-1,3-butadiene, surprisingly we observed only one of the two possible products of 1,2-addition, which arose from attack of the oxy radical at position 2 of the olefin [Eq. (18)]:



Attack of the oxy radical at position 1 led only to products **10** and **11** (*cis* and *trans* isomers) of 1,4-addition, while the product of 1,2-addition was not observed [Eq. (19)]:



The orientation of F-atom addition in position 4 can be explained on the basis of a hypothesis that delocalization of the allylic radical allows the shift of the double bond to the more stable internal position. Moreover according to Eq. (9), the fluorine atom should come from another molecule of hypofluorite; in this case attack at position 4 is also favourable, in comparison to position 2, due to the steric interaction between the incoming hypofluorite and the bulky vicinal $-\text{CF}_2\text{OOCF}_2\text{OOCF}_3$ group.

Finally, hypofluorite **1** appears to be a relatively mild reagent among OF compounds, giving good yields of expected products.

3. Experimental details

3.1. General methods

Volatile compounds were handled in a Pyrex glass or stainless steel vacuum system equipped with a Wallace & Tiernan series 1500 differential pressure gauge. Amounts of gaseous reactants and products were measured assuming ideal gas behaviour. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer connected to a 7500 data station. A 10-cm cell with KCl or AgCl windows was used. ^{19}F NMR spectra were recorded on an IBM NR 200 AF instrument operating at 188.3 MHz, using CFCl_3 as internal reference and CDCl_3 as solvent. Mass spectra were obtained on a Hewlett Packard 5985B spectrometer at 70 eV for CI (CH_4) and EI. GC analysis was carried out on a Perkin-Elmer 8500 (Halocarbon K-352, carrier gas helium). When preparative GC was necessary, a Victoreen 4000 apparatus fitted with a $3\text{ m} \times 1/4$ in column (Halocarbon K-352, carrier gas helium) was used.

3.2. Reagents

Tetrafluoroethylene, chlorotrifluoroethylene, hexafluorobutadiene, 1,2-dichloro-1,2-difluoroethylene, carbon dioxide and carbonyl difluoride were commercial products. Fluorine was passed through an NaF scrubber before use. CsF for the synthesis of compounds **1** and **3** was dried by heating in air with a Bunsen flame in a ceramic crucible for a few hours, then ground in a ball mill under anhydrous conditions. Before reaction it was treated with fluorine (1 atm, room temperature) for 1 h.

3.3. Preparation of $\text{CF}_3\text{OOC(O)F}$ (**3**)

The method reported by DesMarteau was used [7]. Treatment of caesium fluoride as outlined before was essential for a successful reaction; fused and finely ground CsF was too active and led to decomposition of the product to COF_2 and O_2 . The yield of the reaction and the infrared and NMR spectra of this compound corresponded to those reported.

3.4. Preparation of $\text{CF}_3\text{OOCF}_2\text{OF}$ (**1**)

Compound **3** (2–10 mmol) was condensed at -196°C in a 75-ml stainless steel cylinder containing 3 g of CsF treated as described above, then a 10% excess of fluorine was added and the cylinder was placed on frozen CFC-11 and liquid nitrogen. In this way the temperature rose during 16–20 h to -70°C . Excess fluorine was pumped out at -196°C and the product transferred to the vacuum line for measurements. Compound **1** was obtained in quantitative yield and was free of starting material based on IR spectra.

3.5. Reaction of compound **1** with $\text{CF}_2=\text{CFCl}$

In the lower part of a 300 ml cylindrical Pyrex glass vessel, filled with 3/8 in glass beads and fitted with a glass-Teflon valve and a standard taper joint, 7.9 mmol of $\text{CF}_2=\text{CFCl}$ were condensed from the vacuum line at -196°C , the level of the liquid nitrogen was raised and 3.28 mmol of $\text{CF}_3\text{OOCF}_2\text{OF}$ were condensed into the upper part of the reactor. The vessel was placed in an empty Dewar previously cooled with liquid nitrogen, and allowed to return to room temperature overnight. The reaction mixture was fractionated in vacuum through -65°C and -85°C traps, which retained 1.45 mmol of $\text{CF}_3\text{OOCF}_2\text{OCF}_2\text{CF}_2\text{Cl}$ (**6**) and $\text{CF}_3\text{OOCF}_2\text{OCFClCF}_3$ (**7**), through a -95°C trap (empty) and through a -196°C trap, which retained 7.15 mmol of unreacted $\text{CF}_2=\text{CFCl}$, COF_2 and other unidentified products.

Isomers **6** and **7** had the same GC retention time and hence their separation was not possible. From NMR spectral measurements (see Table 1), a ratio of **6** to **7** of 1:1 was ascertained. The following data refer to this 1:1 mixture. IR (cm^{-1}): 1345 (w); 1298 (m); 1256 (vs); 1208 (m); 1136 (vs); 988 (m); 881 (w). MS(CI) (m/e, [fragment], % intensity relative to the parent ion): 101, [CF_3OO], 7.4; 135,

Table 1
NMR data (δ , ppm) of compounds 6–11

	A	B	C	D	E	F
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OF}^{\text{C}}$	–68.9	–80.5	157.5			
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}\text{CF}_2^{\text{D}}\text{Cl}$ (6) ^a	–68.4	–64.8	–88.4	–74.2		
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}\text{ClCF}_3^{\text{D}}$ (7) ^a	–68.3	–63.6	–80.2	–85.8		
		–64.0				
		–64.8				
		–65.2				
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}\text{CF}_3^{\text{D}}$ (8)	–68.3	–64.7	–89.9	–86.9		
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}(\text{CF}_3^{\text{D}})\text{CF}^{\text{E}}=\text{CF}_2^{\text{F}}$ (9)	–68.5	–64.6	–134.2	–84.3	–186	–87
		–65.0				–104
		–66.0				
		–66.4				
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}\text{CF}^{\text{D}}=\text{CF}^{\text{E}}\text{CF}_3^{\text{F}}$ (10) (<i>cis</i> isomer)	–68.3	64.8	–73.6	–158.4	–158.3	–69.2
$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B}}\text{OCF}_2^{\text{C}}\text{CF}^{\text{D}}=\text{CF}^{\text{E}}\text{CF}_3^{\text{F}}$ (11) (<i>trans</i> isomer)	–68.4	64.9	–71.4	–140.7	–141.3	–66.6

^a The two isomers (ratio 1:1) could not be separated.

$[\text{C}_2\text{ClF}_4]$, 55; 151, $[\text{CF}_3\text{OOCF}_2]$ and/or $[\text{C}_2\text{ClF}_4\text{O}]$, 100; 201, $[\text{M}-\text{CF}_3\text{OO}]$, 9; 217, $[\text{M}-\text{CF}_3\text{O}]$, 3.5; 267, $[\text{M}-\text{Cl}]$, 1.6; 283, $[\text{M}-\text{F}]$, 3.6; 303, $[\text{M}+\text{H}]$, 0.5.

3.6. Reaction of compound 1 with $\text{CF}_2=\text{CF}_2$

Using the same procedure as for compounds 6 and 7, 2.26 mmol of 1 were reacted with 4.52 mmol of $\text{CF}_2=\text{CF}_2$. Fractionation gave the following: a -80°C trap retained 1.53 mmol of $\text{CF}_3\text{OOCF}_2\text{OCF}_2\text{CF}_3$ (8) and $\text{CF}_3\text{OOCF}_2\text{CF}_2\text{OCF}_3$ in a 8:2 ratio (the byproduct was identified from its known NMR spectrum [3]) a -196°C trap retained 2.41 mmol of volatiles that had passed through a -100°C trap (IR spectral analysis showed that this fraction contained C_2F_4 and COF_2 , and the NMR spectrum also showed $\text{CF}_3\text{OOC}_2\text{F}_5$, $\text{CF}_3\text{OC}_2\text{F}_5$, CF_3OOCF_3 , $\text{CF}_3\text{OOOCF}_3$, all known compounds [3,4,7]). Only traces of C_2F_4 polymer and no uncondensable gases were found.

$\text{CF}_3\text{OOCF}_2\text{OCF}_2\text{CF}_3$ (8): NMR (see Table 1). IR (cm^{-1}): 1256 (vs); 1202 (s); 1172 (s); 1142 (vs); 1107 (sh.); 893 (w); 756 (w); 722 (w). MS(CI) (*m/e*, [fragment], % intensity relative to the parent ion): 101, $[\text{CF}_3\text{OO}]$, 9.8; 119, $[\text{C}_2\text{F}_5]$, 27; 151, $[\text{M}-\text{C}_2\text{F}_5]$, 100; 185, $[\text{M}-\text{CF}_3\text{OO}]$, 26.4; 267, $[\text{M}-\text{F}]$, 59. Analysis: Calc. for $\text{C}_4\text{F}_{10}\text{O}_3$: C, 16.80; F, 66.42%. Found: C, 17.23; F, 65.34%.

3.7. Reaction of compound 1 with $\text{CF}_2=\text{CF}=\text{CF}=\text{CF}_2$

Following the previously reported procedure, 1.75 mmol of 1 were reacted with 5.22 mmol of $\text{CF}_2=\text{CF}=\text{CF}=\text{CF}_2$. Fractionation in a -48°C and -76°C trap gave a total amount of 1.30 mmol of product. By GC and NMR analysis, this fraction contained three products. The reaction was repeated to provide more for separation. From gas chromatography, it was apparent that the products, injected as liquids, decomposed upon injection into more volatile compounds; by lowering the temperature of the injection port to 100°C

from the usual 200°C and operating the column below 100°C , such decomposition was reduced. Under these conditions, preparative GC (isothermal, 80°C) allowed the separation of $\text{CF}_3\text{OOCF}_2\text{OCF}(\text{CF}_3)\text{CF}=\text{CF}_2$ (9) from *cis*- $\text{CF}_3\text{OOCF}_2\text{OCF}_2\text{CF}=\text{CFCF}_3$ (10) and the *trans* isomer (11) (not baseline separated). The properties of the isolated compounds are listed below.

Compound 9: IR (cm^{-1}): 1787 (m); 1346 (m); 1310 (s); 1238 (vs); 1154 (s); 1096 (m); 956 (w); 880 (w). MS(CI) (*m/e*, [fragment], % intensity relative to the parent ion): 151, $[\text{M}-\text{C}_4\text{F}_7\text{O}]$, 6.7; 181, $[\text{C}_4\text{F}_7]$, 100; 247, $[\text{M}-\text{CF}_3\text{OO}]$, 2.1; 263, $[\text{M}-\text{CF}_3\text{O}]$, 3.7; 329, $[\text{M}-\text{F}]$, 14.2. Analysis: Calc. for $\text{C}_6\text{F}_{12}\text{O}_3$: C, 20.70; F, 65.50%. Found: C, 20.63; F, 65.89%.

Compound 10: IR (cm^{-1}): 1786 (w); 1255 (vs); 1187 (s); 1138 (s); 959 (w); 858 (w). Analysis: Calc. for $\text{C}_6\text{F}_{12}\text{O}_3$: C, 20.70; F, 65.50%. Found: C, 20.57; F, 66.22%.

Compound 11: IR (cm^{-1}): 1727 (m); 1350 (m); 1251 (vs); 1190 (vs); 1176 (vs); 973 (w); 949 (w); 872 (w); 820 (w). Analysis: Calc. for $\text{C}_6\text{F}_{12}\text{O}_3$: C, 20.70; F, 65.50%. Found: C, 20.51; F, 65.05%. For NMR data: see Table 1.

In this reaction, the other possible isomer from 1,2-addition to one double bond, i.e. $\text{CF}_3\text{OOCF}_2\text{OCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, was never observed.

3.8. Reaction of compound 1 with $\text{CFCl}=\text{CFCl}$

A general method for the semicontinuous addition of 1 to $\text{CFCl}=\text{CFCl}$ was as follows. Into a 50 ml Pyrex glass reactor, connected to a Pyrex-glass vacuum system, $\text{CFCl}=\text{CFCl}$ (4 mmol) was condensed at -196°C . The reactor was then placed in a CFC-11 bath kept at the desired temperature (-60 to -100°C). Within this temperature range the vapour pressure of the olefin was lower than 8 mbar. Compound 1 (1 mmol) was then condensed at -196°C [with F_2 (0.1 mmol) if used] in a trap connected to the reactor by a vacuum line. The latter was then warmed up to -105°C . At this temper-

Table 2
Product yield in the reaction of compound **1** with $\text{CFCl}=\text{CFCl}$ in the absence of F_2

Reaction temp. (°C)	Product yield (%) ^a	
	$\text{CF}_3\text{OOCF}_2\text{OCFCICF}_2\text{Cl}$	Dioxolane (<i>cis</i> + <i>trans</i>)
–60	27	24
–100	67	7

^a Determined by NMR spectroscopy (% referred to hypofluorite).

ature the vapour pressure of **1** was ca. 25 mbar. The hypofluorite was allowed to transfer from the trap to the reactor. The rate of addition could be controlled by a valve and was complete over a period of 0.5. The products were separated by trap-to-trap distillation and characterized by NMR, IR and mass spectroscopy. NMR yields for the two major reaction products of the reactions carried out when fluorine was not present are summarized in Table 2.

$\text{CF}_3^{\text{A}}\text{OOCF}_2^{\text{B,B'}}\text{OCF}^{\text{C}}\text{CICF}_2^{\text{D,D'}}\text{Cl}$: ^{19}F NMR: $\delta_{\text{A}} = -68.2$ (t) ppm; $\delta_{\text{B,B'}}$ (AB system) = -63.6 (m), -63.9 (m), -64.8 (m), -65.1 (m) ppm; $\delta_{\text{C}} = -76.93$ (m) ppm; $\delta_{\text{D,D'}}$ = -70.87 (d,d) ppm; $J_{\text{AB}} = 3.7$ Hz; $J_{\text{BC}} = 11.9$ Hz; $J_{\text{CD}} = 5.9$ Hz; $J_{\text{BB'}} = 220.5$ Hz; $J_{\text{DD'}} = 6.9$ Hz. IR (cm^{-1}): 1293 (s); 1251 (vs); 1215 (vs); 1134 (vs); 1043 (m); 893

(m); 845 (m). MS(CI) (m/e , [fragment], % intensity relative to parent ion): 69, $[\text{CF}_3]$, 100; 101, $[\text{CF}_3\text{OO}]$, 32.7; 151, $[\text{C}_2\text{Cl}_2\text{F}_3]$ and/or $[\text{CF}_3\text{OOCF}_2]$, 27.9; 217, $[\text{C}_3\text{Cl}_2\text{F}_5\text{O}]$, 29.9. Analysis: Calc. for $\text{C}_4\text{Cl}_2\text{F}_8\text{O}_3$: C, 15.06; Cl, 22.23; F, 47.65%. Found: C, 15.24; Cl, 22.56; F, 46.53%.

$\text{CF}^{\text{C}}\text{Cl}-\text{CF}^{\text{C}}\text{Cl}-\text{OCF}_2^{\text{A,B}}\text{O}$ *trans* [8,10]: ^{19}F NMR: $\delta_{\text{A}} = \delta_{\text{B}} = -55.5$ (t) ppm; $\delta_{\text{C}} = -57.7$ (t) ppm; $J_{\text{BC}} = J_{\text{AC}} = 5$ Hz.

$\text{CF}^{\text{C}}\text{Cl}-\text{CF}^{\text{C}}\text{Cl}-\text{OCF}_2^{\text{A,B}}\text{O}$ *cis* [8,10] ^{19}F NMR: δ_{AB} (AB system) = -55.4 (d), -58 (dt) ppm; $\delta_{\text{C}} = -69.9$ (d) ppm; $J_{\text{BC}} = 9$ Hz; $J_{\text{AB}} = 68$ Hz.

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