Direct Synthesis of Fluorocarbon Peroxides. I. Addition of Bis(trifluoromethyl) Trioxide to Selected Carbon–Carbon Multiple Bonds[1,2]

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The addition of bis(trifluoromethyl) trioxide, CF_3OOOCF_3, to a variety of carbon–carbon multiple bonds is reported. With ethylene, tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene, perfluorobutene-2, and perfluorocyclopentene the usual products are $CF_3OOCR_1R_2CR_3R_4OCF_3$ and $CF_3OCR_1R_2CR_3R_4OOCF_3$. These products form in 50–80% yield with alkenes which are not prone to radical polymerization. In the case of tetrafluoroethylene and chlorotrifluoroethylene, additional products containing 2 mol of alkene are observed as well as several trifluoromethyl ethers. The proposed reaction mechanism of initial addition of $CF_3O\cdot$ to the alkene is consistent with the observed products.

Fluorocarbon peroxides are an interesting class of potentially useful compounds. However, until quite recently, examples of these compounds were very limited because of the lack of any general synthetic methods. Previously, most compounds of this type were obtained by reactions involving the coupling of two oxy radicals to form a peroxide bond.[3] The utility of such reactions is severely limited by the apparent instability of most perfluoroalkoxy radicals. The synthesis of trifluoromethyl hydroperoxide in 1968[4] and subsequent development of its chemistry[5-9] indicated that a more successful route to fluorocarbon peroxides containing the CF_3OO group lay in the direct addition of this moiety to suitable substrates. Now several other methods of general synthetic value, in which the CF_3OO group is introduced as a unit, have been found. These involve reactions of fluoroperoxytrifluoromethane (CF_3OOF),[10] chloroperoxytrifluoromethane (CF_3OOCl),[11] and bis(trifluoromethyl) trioxide (CF_3OOOCF_3),[12] as shown in the following general equations.

$$CF_3OOF + R_1R_2C{=}CR_3R_4 \longrightarrow CF_3OOCR_1R_2CR_3R_4F$$

$$CF_3OOCl + R_1R_2C{=}CR_3R_4 \longrightarrow CF_3OOCR_1R_2CR_3R_4Cl$$

$$CF_3OOOCF_3 + R_1R_2C{=}CR_3R_4 \longrightarrow CF_3OOCR_1R_2CR_3R_4OCF_3$$

$$R = H, F, Cl, \text{alkyl, or perfluoroalkyl}$$

$$CF_3OOOCF_3 + X \longrightarrow CF_3OOXOCF_3$$

$$X = SO_2, SF_4, CO$$

In this paper, additions of CF_3OOOCF_3 to a variety of olefins, forming new compounds of the type CF_3OO-$CR_1R_2CR_3R_4COCF_3$ and $CF_3OCR_1R_2CR_3R_4OOCF_3$, are described. Evidence is presented for the radical nature of these reactions involving the initial addition of $CF_3O\cdot$ to the alkene.

Results and Discussion

The addition of bis(trifluoromethyl) trioxide to alkenes is a new general route to fluorocarbon peroxides. Although we encountered one failure, that with cyclopentene, the others attempted did give the expected 1:1 addition products as shown in Table I. The molecular weight and ir data indicate the empirical formulas, while the nmr data in Table II identify the isomers present. The group shift for CF_3OO- at $\phi^* \sim 69$ and CF_3O- at $\phi^* \sim 56$ are quite characteristic of these new compounds. Decoupling of nmr spectra was particularly informative in deducing structures. The more stable, highly fluorinated alkenes, which are not as prone to polymerization, gave very good yields. The mechanism for formation of these products is probably a free-radical chain of the type shown.

$$CF_3OOOCF_3 \xrightarrow[\Delta]{\sim 70°} CF_3OO\cdot + CF_3O\cdot \quad (1)$$

$$2CF_3OO\cdot \longrightarrow [CF_3OOOOCF_3] \longrightarrow CF_3OOCF_3 + O_2 \quad (2)$$

$$CF_3O\cdot + R_1R_2C{=}CR_3R_4 \longrightarrow CF_3OR_1R_2C{-}\dot{C}R_3R_4 \quad (3)$$

$$CF_3O\cdot + R_1R_2C{=}CR_3R_4 \longrightarrow R_1R_2\dot{C}{-}CR_3R_4OCF_3 \quad (4)$$

$$CF_3OR_1R_2C{-}\dot{C}R_3R_4 + CF_3OOOCF_3 \longrightarrow CF_3OR_1R_2C{-}CR_3R_4OOCF_3 + CF_3O\cdot \quad (5)$$

$$R_1R_2\dot{C}{-}CR_3R_4OCF_3 + CF_3OOOCF_3 \longrightarrow CF_3OOR_1R_2C{-}CR_3R_4OCF_3 + CF_3O\cdot \quad (6)$$

$$CF_3O\cdot + CF_3O\cdot + M \longrightarrow CF_3OOCF_3 + M^* \quad (7)$$

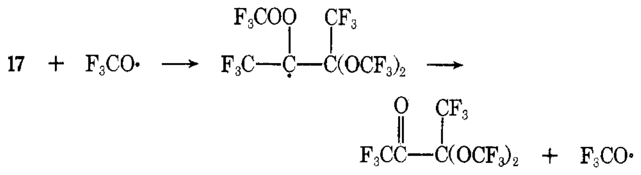
$$M = \text{reactor walls or a gas}$$

This mechanism is consistent with (1) the evidence for polymerization which suggests the presence of free radicals; (2) the necessity to heat the reactions to about 70°, at which temperature the trioxide decomposes slowly to CF_3OOCF_3 and O_2; (3) the known dissociation of peroxides, trioxides, and tetraoxides into oxy and peroxy radicals,[13] and (4) production of the observed new compounds.

Our choice of which compounds to designate erythro and threo between **11** and **12** and cis and trans between **13** and **14** is somewhat arbitrary. By application of Cram's rule, we have determined that the more abundant isomer between **11** and **12** should be erythro. Hence, we have designated **11** as *erythro*-1,2,3,3,3-pentafluoro-1-trifluoromethyl-2-(trifuoromethyldioxy)propyl trifluoromethyl ether. In the case of **13** and **14**, larger coupling constants are observed between ring substituents that are trans to each other. Hence, we have designated **14** *trans*-1,2,3,3,4,4,5,5-octafluoro-2-(trifluoromethyldioxy)cyclopentyl trifluoromethyl ether.

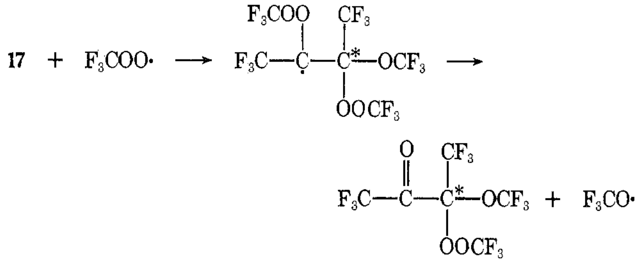
The reaction of CF_3OOOCF_3 with the perfluoroalkyne, $CF_3C{\equiv}CCF_3$, proceeds with extensive polymerization which may physically entrap the expected product making isolation impossible. The products we do observe, **15** and **16**, are not as well characterized as the products from reaction with alkenes. On the basis of its nmr, **16** could have the structure *trans*-$(CF_3O)(CF_3)C{=}C(CF_3)(OOCF_3)$ (**17**), although our molecular weight and ir data suggest the structure we have given. **17** is the initial hypothetical product resulting from addition of the elements of CF_3OOOCF_3 to $CF_3C{\equiv}CCF_3$ which could then undergo further reaction to give **15** and **16** as shown.

The incorporation of more than 1 mol of alkene in the products from reaction of CF_3OOOCF_3 with C_2F_3Cl and C_2F_4 results in nmr spectra that are difficult to interpret.



$$\mathbf{17} + F_3CO\cdot \longrightarrow F_3C\text{—}\overset{F_3COO}{\dot{C}}\text{—}\overset{CF_3}{C}(OCF_3)_2 \longrightarrow F_3C\overset{O}{\overset{\|}{C}}\text{—}\overset{CF_3}{C}(OCF_3)_2 + F_3CO\cdot$$

15



$$\mathbf{17} + F_3COO\cdot \longrightarrow F_3C\text{—}\overset{F_3COO}{\dot{C}}\text{—}\underset{OOCF_3}{\overset{CF_3}{C^*}}\text{—}OCF_3 \longrightarrow F_3C\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{OOCF_3}{\overset{CF_3}{C^*}}\text{—}OCF_3 + F_3CO\cdot$$

16

Nonetheless, the reaction and its mechanistic implications deserve further consideration. In a previous paper,[11] we postulated a mechanism for addition of CF_3OOOCF_3 to central atoms in which one initial step was addition of $CF_3OO\cdot$ to the central atom. The observed reaction products of C_2F_3Cl in this work make such a step improbable. In the reaction of C_2F_3Cl we observe 1:1 isomers, V and VI. If a step in their formation is $CF_3OO\cdot + C_2F_3Cl \rightarrow CF_3OOCFClCF_2\cdot$ and $CF_3OOCF_2CFCl\cdot$, then as 2:1 products we would expect to observe both $CF_3O\text{-}OCFClCF_2(C_2F_3Cl)OCF_3$ (**8**, a mixture of isomers) and $CF_3OOCF_2CFCl(C_2F_3Cl)OCF_3$. The nmr of the 2:1 product shows only CF_3OO peaks split into doublets. We attribute this to the various isomers of **8**. The ethers, **7**, are also a mixture of isomers. These observations lead us to postulate the additional steps in the cases of C_2F_3Cl where $R_1 = R_2 = R_3 = F$ and $R_4 = Cl$ (similar considerations apply to the reaction with C_2F_4 with appropriate allowance for the higher symmetry of the alkene).

$$CF_3OCFCl\dot{C}F_2 + C_2F_3Cl \longrightarrow CF_3OCFClCF_2CF_2\dot{C}FCl \quad (8)$$

$$CF_3OCF_2\dot{C}FCl + C_2F_3Cl \longrightarrow CF_3OCF_2CFClCF_2\dot{C}FCl \quad (9)$$

$$CF_3OCFClCF_2CF_2\dot{C}FCl + CF_3OOOCF_3 \longrightarrow \mathbf{8} + CF_3O\cdot \quad (10)$$

$$CF_3OCF_2CFClCF_2\dot{C}FCl + CF_3OOOCF_3 \longrightarrow \mathbf{8} + CF_3O\cdot \quad (11)$$

$$2CF_3OCF_2\dot{C}FCl + M \longrightarrow \mathbf{7} + M^* \quad (12)$$

$$2CF_3OCFCl\dot{C}F_2 + M \longrightarrow \mathbf{7} + M^* \quad (13)$$

$$CF_3OCF_2\dot{C}FCl + CF_3OCFCl\dot{C}F_2 + M \longrightarrow \mathbf{7} + M^* \quad (14)$$

$$CF_3OCFClCF_2CF_2\dot{C}FCl + CF_3O\cdot + M \longrightarrow \mathbf{7} + M^* \quad (15)$$

$$CF_3OCF_2CFClCF_2\dot{C}FCl + CF_3O\cdot + M \longrightarrow \mathbf{7} + M^* \quad (16)$$

This chain process is a specific form of the general equations for addition to C-C double bonds. In it, CF_3OOOCF_3 is a good transfer agent because the rates of steps 5 + 6 and 10 + 11 are apparently greater than subsequent alkene addition steps would be. Consequently, telomers of relatively low molecular weight are observed. Although reaction of excess alkene with CF_3OOOCF_3 should result in formation of $CF_3O(C_2F_3Cl)_nOCF_3$, we did not attempt such a reaction because of experimental difficulties we would encounter attempting to characterize the products. Small amounts of these products may have been present under our conditions and were not identified.

The high yields we obtain with several of the alkenes tried demonstrates that the reaction is quite specific. We believe that this specificity is in steps 5, 6, 10, and 11 where reaction of a free radical with CF_3OOOCF_3 occurs

Table I
Reaction of CF_3OOOCF_3 with C=C and C≡C

	$R_1R_2C{=}CR_3R_4$						Conditions		Products				Log $P_{(t)} = A - B/T - C/T^2$		
Registry no.	R_1	R_2	R_3	R_4	*a*	CF_3OOOCF_3[a]	Temp, °C	Time, hr	No.	Mol wt (calcd)	Yield,[b] %	Bp, °C	*A*	*B*	*C*
74-85-1	H	H	H	H	4.46	4.46	65	3	**1**	211.8 (214.1)	14	73.9[c]	8.706	2022	
116-14-3	F	F	F	F	2.08	2.20	73	3	**2**	288.4 (286.0)	8	33.6	7.848	1542	
									3	345 (370)	2.5				
									4	360 (386)	9				
79-38-9	F	F	F	Cl	4.64	5.57	69	1	**5, 6**	300 (302.5)	4	54.8[c,d]	8.194	1743	
									7	412 (403)	4		21.3 *t*	19.7°[d]	
									8	423 (419)	3		16.8 *t*	20.0°[d]	
116-15-4	F	F	F	CF_3	4.24	4.49	67	3	**9, 10**	336.8 (336.0)	52	51.9[d]	61.118	488.60	18,300
360-89-4	F	CF_3	F	CF_3	3.90	4.43	67	4	**11, 12**	380.6 (386.0)	68	72.0[c,d]	6.6756	838.56	15,670
559-40-0	$c\text{-}C_5F_8$				4.85	5.97	67	8	**13, 14**	399.5 (398.0)	80	91.2[c,d]	5.2858	21.833	32,730
	$c\text{-}C_5H_8$				4.46	5.26	68	0.5							
692-50-2	$CF_3C{\equiv}CCF_3$				4.00	8.14	65	1.5	**15, 16**	360 (*cf.* text)	8				

[a] Amounts in millimoles. [b] Based on amount of alkene. [c] Extrapolated from values at lower temperatures. [d] Isomers present; refer to Table II.

Table II
Nmr Data

Compd	Formula[a]	Chemical shift[b]						Selected coupling constants[c]
		A	B	C	D	E	F	
1	$CF_3OOCH_2CH_2OCF_3$ A B C D	68.56 m	4.555[d] m	4.307[d] m	62.51 m			AB = 0.8, BC = 3.42,[d] BC′ = 6.14[d] CD = 0.5, BB′CC′ = 1.66[d]
2	$CF_3OOCF_2CF_2OCF_3$ A B C D	68.69 t	96.37 q, q	87.03 q	55.98 t, t			AB = 4.4, BD = 0.6, CD = 9.0
3	$CF_3OCF_2CF_2CF_2CF_2OCF_3$ A B C C B A	55.80 t	85.84 m	126.12 m				AB = 9.2, BC = 0.4, BC′ = 7.5
4	$CF_3OOCF_2CF_2CF_2CF_2OCF_3$ A B C D E F	68.78 t	90.69 m	123.54 m	125.96 m	85.60 m	55.87 t	AB = 4.3, BC = 2.2, BD = 9.2, BE = 0.4, CE = 10.3, DE = 0.5, EF = 9.1
5	$CF_3OOC{*}FClCF_2OCF_3$ A B CD E	68.45 d	83.09 m	84.60 m	84.6 m	56.37 d, t		AB = 5.1, BC = BD = 4.4, BE = 0.6, CE = DE = 9.1
6	$CF_3OOCF_2C{*}FClOCF_3$ A BC D E	68.99 t	94.26 m	94.36 m	77.34 m	55.56 d, t		AB = AC = 4.5, BD = 4.0, CD = 5.0, BE = CE = 0.6, DE = 10.1
7	$(CF_3O)_2(CF_2\overset{*}{C}FCl)_2$ ABC	55.31 d	56.15 d	56.17 t				A = 10.0, B = 9.8, C = 9.0
8	$CF_3OOC{*}FClCF_2(CF_2\overset{*}{C}FCl)OCF_3$ AB CDE	67.84 d	67.96 d	55.09 d	55.94 t	55.98 t		A = 4.8, B = 4.9, C = 10.2, D = 9.2, E = 9.0
9	$CF_3OOC{*}F(CF_3)CF_2OCF_3$ A B C DE F	69.34 d	139.01 m	76.48 t	81.35[e] m	81.35[e] m	56.50 t	AB = 6.2, BD = BE = 4.8, CD = CE = 9.0, DF = CF = 9.0
10	$CF_3OOCF_2C{*}F(CF_3)OCF_3$ A BC D E F	69.44 t	90.74[e] m	90.74[e] m	144.43 m	81.38 m	54.83 d, m	AB = AC = 4.4, BD = CD = 4.1, BE = CE = 8.6, BF = CF = 4.0, EF = 4.0
11	*erythro*- $CF_3OOC{*}F(CF_3)C{*}F(CF_3)OCF_3$ A B C D E F	68.69 d	154.53 m	74.15 sex, m	140.23 m	79.32 m	53.53 m	AB = 6.2, BF = 5.4, C = 11.5 d, C = 5.2 q, CF = 1.6, DF = 15.8, EF = 5.4
12	*threo*- $CF_3OOC{*}F(CF_3)C{*}F(CF_3)OCF_3$ A B C D E F	68.66 d	133.37 m	73.69 d, m	137.16 m	77.68 m	54.35 m	AB = 6.2, BF = 1.7, CF = 1.7, DF = 13.6, EF = 7.2
13	*cis*-$CF_3OOC_5F_8OCF_3$ A B	68.59 d	55.72 m					A = 6.6 d, B = 10.5 d, 8.5 d, 5.0 d, 2.2 d, AB ~0.2
14	*trans*-$CF_3OOC_5F_8OCF_3$ A B	68.60 d	55.14 m					A = 6.1 d, B = 12.0 d, 8.2 d, 5.0 d, 3.2 d, AB ~0.4
15	$(CF_3O)_2C(CF_3)C(O)CF_3$ A B C	54.35 q, q	76.53 m	73.61 q, sep				AB = 4.9, AC = 1.1, BC = 3.7
16	$CF_3OO{*}C(OCF_3)(CF_3)C(O)CF_3$ A B C D	68.12 m	54.53 m	73.68 m	74.34 m			AB = 1.9, AC = 0.7, AD = 1.2, BC = 1.2, BD = 2.4, CD = 3.8

[a] An asterisk denotes a chiral center. In **7** and **8** the ABC, CDE, and AB refer to the different CF_3O and CF_3OO groups of the various isomers. [b] Values are ϕ^* for ^{19}F and δ for ^1H, both in parts per million, to center of peak or multiplet: d = doublet, t = triplet, q = quartet, sex = sextet, sep = septet, m = multiplet. [c] J_{AB} = 0.0 Hz is abbreviated AB = 0.0 and refers to coupling between fluorines designated A and B; A = 10.0, etc., refers to the fluorine designated A coupled to another unspecified fluorine(s). [d] Values are from computer-assisted solution of the experimental spectrum. [e] A difference between the fluorines of this CF_2 group could not be observed.

to abstract the CF_3OO moiety and generate a new radical, $CF_3O\cdot$. In the reaction of hexafluoropropene, formation of **9** in preference to **10** (71 to 29%) is suggestive. Addition of radicals to an alkene is predicted to occur so as to form the more stable free radical.[14] In this instance, formation of $CF_3OCF_2\dot{C}FCF_3$ should be preferred over formation of $CF_3OCF(CF_3)\dot{C}F_2$. This is consistent with the observed production of **9** and **10**, presumably by further reaction of the respective radicals above.

This role of CF_3OOOCF_3 as a transfer agent is perhaps better considered with greater perspective. The more common transfer agents are the halogens, and CF_3OOOCF_3 can be viewed as a halogenoid. It is a volatile compound but not as symmetric as the more common pseudohalogens such as $(CN)_2$, $(OCN)_2$, $(SCN)_2$, $(OSO_2F)_2$, etc. Salts with the formulas $MOCF_3$ are known and those of $MOOCF_3$ have been postulated.[7,15] The free acid, CF_3OOH, is known[4,5] and derivatives of CF_3OH are well known.[16] A halogenoid's radicals may react with other halogens, forming compounds such as CF_3OOF,[7] CF_3OF,[17] CF_3OOCl,[8] CF_3OCl,[18,19] etc. A halogenoid adds to alkenes and to central atoms in a low oxidation state. In this light, it is instructive to view CF_3OOCF_3 as an interhalogenoid.

All of the new peroxides obtained in this work are stable for prolonged periods at 22°. None have been observed to be explosive (Caution! potential explosive decomposition is possible for any of these compounds) and they are easily handled in both glass and metal equipment. While detailed stability studies have not been made on these new materials, their apparent high thermal stabilities clearly demonstrate the stabilizing effect of fluorine in such compounds Most hydrocarbon analogs of these compounds, if known, would not be expected to have high thermal stabilities in view of the C:O ratios. The addition of CF_3OOOCF_3 to olefins is clearly a new and useful reaction for the formation of fluorocarbon peroxides. In our opinion, extension of this reaction to many other alkenes is possible, particularly fluoroalkenes. Failure of this reaction to give the expected products will probably occur in some cases owing to carbon–carbon bond cleavage as observed with cyclopentene. However, moderation of the reaction conditions using radical initiators at lower temperatures might offer a method of overcoming these failures.

Experimental Section

General. All work was carried out on a standard vacuum line.[20] Quantities of reactants and products were measured either by direct weighing or by the relationship $n = PV/RT$, assuming ideal gas behavior. All reactions were carried out in 100–500-ml Pyrex bulbs fitted with a Kontes K-82600 Teflon-glass valve. Reaction products were usually given a preliminary separation through U traps cooled to an appropriate temperature. Following this, the products were separated *via* glc on a Victoreen Series 4000 gas chromatograph equipped for gas or liquid injection, sub- or superambient operation, thermal conductivity detection, and low-temperature collection. A 10 ft × 0.375 in. column of 304 stainless steel packed with 49% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P was used in most cases. For less volatile products, a 1-ft column of similar construction was used.

Structural determinations were made on a Varian XL-100-15 nmr spectrometer. Interpretation of nmr spectra was aided by a computer program, LAOCOON 3.[21]

In reactions giving high yields, vapor pressures and boiling points of the products were measured by the method of Kellogg and Cady.[17] Similar data for other products were obtained by a static method. In either case, temperatures were measured with a calibrated iron-constantan thermocouple and pressures were measured with a Wallace and Tiernan Model FA 145 differential pressure gauge. This gauge was also used to measure pressures for molecular weight determinations by vapor density.

Infrared spectra were recorded on Perkin-Elmer Model 180 or Model 337 spectrometers. Mass spectra were obtained on an AEI MS9 spectrometer at 70 eV with a source temperature of 200°. The base peak in all instances was at m/e 69 (CF_3^+).

Reagents. Bis(trifluoromethyl) trioxide was prepared by reaction of a $CsOCF_3$–CsF mixture with OF_2 at 42° as previously described.[12,22] It was purified by repeated low-temperature trap-to-trap distillation until free from CF_3OOF as evidenced by ir at 950 cm^{-1} in a 10-cm cell at 100 Torr total pressure. Tetrafluoroethylene was prepared by thermal degradation of Teflon.[23] Chlorotrifluoroethylene, hexafluoropropene, perfluorobutene-2 (20.4% cis *via* nmr), perfluorocyclopentene, and hexafluorobutyne-2 were obtained from PCR, Inc. The C_2F_3Cl was passed through a −78° bath before use to remove its inhibitor; the others contained no such inhibitor and were used as received. Cyclopentene was obtained from Aldrich and used as received. Likewise, C_2H_4 from Matheson Gas Products was used as supplied.

The experimental conditions for preparation of these new ethers and peroxides are given in Table I. Nmr values characterizing the products are contained in Table II. No attempts were made to separate the various pairs of isomers encountered in this work. In all reactions, polymerization of the alkene or alkyne apparently occurred, as evidenced by the formation of a nonvolatile oil or white solid which was not characterized further. Several low molecular weight products were observed in these reactions as well. These included O_2 and CF_3OOCF_3 in all reactions with minor amounts of COF_2 and SiF_4. With C_2F_3Cl considerable CF_2CFClO was observed.

Reaction of C_2H_4. This reaction readily gives 2-[(trifluoromethyl)dioxy]ethyl trifluoromethyl ether (**1**) plus additional products, some of which were polymeric. Heteronuclear INDOR decoupling shows that both CH_2 groups are coupled to both CF_3 groups. Heteronuclear noise decoupling results in a symmetrical AA′BB′ ^1H spectrum whose computed solution is given in Table II: ir 2996 sh, 2968 m, 2944 m, 1469 m, 1414 m, 1378 m, 1339 m, 1280 vs, 1229 vvs, 1171 vs, 1119 m, 1080 m, 1050 m, 1009 m, 929 m, 879 m, 860 m, 820 m, 679 m, 619 m, 588 m, 510 cm^{-1} m.[20]

Reaction of C_2F_4. Extensive polymerization apparently occurs as evidenced by formation of a nonadhering white solid in the reaction. We have identified the following products: 1,1,2,2,-tetrafluoro-2-[(trifluoromethyl)dioxy]ethyl trifluoromethyl ether (**2**), ir 1382 m, 1290 vs, 1251 vvs, 1203 s, 1178 s, 1148 vs, 1089 s, 900 s, 803 m, 683 m, 671 m, 606 m, mass spectrum (selected values) m/e (rel intensity, assignment) 151 (2.0, $C_2F_5O_2$), 135 (11.4, C_2F_5O), 119 (14.6, C_2F_5), 97 (7.3, C_2F_3O); 1,1,2,2,3,3-hexafluoro-1,3-bis(trifluoromethoxy)propane, ir 1330 s, 1286 vs, 1268 sh, 1248 vvs, 1211 vs, 1197 sh, 1188 sh, 1182 vs, 1160 vvs, 1130 vs, 1096 m, 963 m, 928 m, 893 m, 861 m, 807 m, 793 m, 681 m, 657 m, 621 m, 586 cm^{-1} m; 1,1,2,2,3,3,4,4-octafluoro-4-[(trifluoromethyl)dioxy]butyl trifluoromethyl ether (**4**), ir 1365 m, 1289 vs, 1248 vvs, 1215 vs, 1185 sh, 1160 vvs, 1088 s, 958 m, 931 m, 913 m, 899 m, 883 m, 869 s, 841 m, 823 m, 793 s, 778 s, 728 m, 678 m, 653 m, 628 m, 610 m, 575 cm^{-1} m.[20]

Reaction of C_2F_3Cl. Extensive polymerization and formation of several new compounds are observed. We have identified the following: 2-chloro-1,1,2-trifluoro-2-[(trifluoromethyl)dioxy]ethyl trifluoromethyl ether (**5**) and 1-chloro-1,2,2-trifluoro-2-[(trifluoromethyl)dioxy]ethyl trifluoromethyl ether (**6**). The asymmetric carbon atom in these compounds results in the fluorines of the adjacent CF_2 group being nonequivalent. This nonequivalence gives rise to an ABX nmr spectrum: ir (85% **5**, 15% **6**) 1331 s, 1291 vs, 1274 s, 1248 vvs, 1212 vs, 1164 vs, 1152 s, 1073 s, 1000 m, 938 m, 919 m, 893 m, 865 m, 852 m, 818 m, 769 m, 746 m, 661 m, 605 m, 591 cm^{-1} m; mass spectrum m/e (rel intensity, assignment) 267 (1.0, $C_4F_9O_3$), 217 (0.7, $C_3F_6O_2Cl$), 201 (1.8, C_3F_6OCl), 167 (1.7, $C_2F_4O_2Cl$), 151 (2.9, $C_2F_5O_2$), 147 (2.6, C_3F_5O), 135 (16, C_2F_4Cl), 131 (1.9, C_3F_5), 119 (2.7, C_2F_5), 100 (1.5, C_2F_4), 97 (7.9, C_2F_3O), 85 (5.2, CF_3O, CF_2Cl).[20]

Dichlorohexafluoro-1,4-bis(trifluoromethoxy)butane (7). The possibility of three structural isomers, each having two asymmetric carbon atoms, gives rise to six possible structures. Since we observe a very complex nmr having at least three unique CF_3O groups, a more specific description of the product is not possible. The area ratio of the CF_3O groups (A:B:C) is 1:1.3:4.4 *via* nmr: ir of the mixture 1308 s, 1243 vvs, 1148 vs, 1069 m, 990 m, 960 m, 885 m, 864 m, 842 m, 813 m, 778 m, 681 m, 660 m, 609 cm^{-1} m.

Dichlorohexafluoro-4-[(trifluoromethyl)dioxy]butyl Trifluoromethyl Ether (8). As in the case of **7**, two asymmetric carbon atoms are present in the molecules. The nmr spectrum, although still very complex, does permit us to specify the molecules as being 4-chloro-3,3,4-trifluoro, since the two CF_3OO peaks observed are split into 1:1 doublets. The area ratio of these CF_3OO peaks (A:B) is 1.4:1.0: ir of the mixture 1316 s, 1292 vs, 1245 vvs, 1195 sh, 1148 vs, 1073 sh, 999 m, 967 m, 882 m, 818 m, 779 m, 762 m, 716 m, 663 m.[20]

Reaction of C_3F_6. High yields of the 1:1 addition product are obtained in which both isomers are observed *via* nmr. We have identified 1,1,2,3,3,3-hexafluoro-2-[(trifluoromethyl)dioxy]propyl trifluoromethyl ether (**9**) and trifluoromethyl 1,2,2-trifluoro-1-(trifluoromethyl)-2-[(trifluoromethyl)dioxy]ethyl ether (**10**): ir (71% **9**, 29% **10**) 1338 s, 1328 s, 1291 vs, 1278 vs, 1255 vvs, 1225 s, 1212 vs, 1165 s, 1142 vs, 1110 s, 1035 m, 1018 m, 990 m, 938 m, 898 m, 862 m, 828 m, 772 m, 748 m, 714 m, 684 m, 676 m, 658 m, 624 m, 542 cm^{-1} m; mass spectrum *m/e* (rel intensity, assignment) 201 (1.6, $C_3F_2O_2$), 185 (1.2, C_3F_7O), 170 (2.5, $C_2F_6O_2$), 151 (1.3, $C_2F_5O_2$), 147 (5.1, C_3F_5O), 135 (14.5, C_2F_5O), 119 (3.3, C_2F_5), 97 (7.6, C_2F_3O).[20]

Reaction of C_4F_8. A high yield of the expected 1:1 addition product is obtained. Since there are two asymmetric carbon atoms, an erythro and threo structure can be formed and indeed two molecules containing six peaks each are observed in the nmr. The most obvious difference in their nmr spectra is the appearance of the CF_3 absorptions at 73.69 and 74.15 ppm. The former is basically a doublet; the latter is a sextet formed from an overlapping doublet of quartets, *erythro*-1,2,3,3,3-Pentafluoro-1-(trifluoromethyl)-2-[(trifluoromethyl)dioxy]propyl trifluoromethyl ether (**11**) and *threo*-1,2,3,3,3-pentafluoro-1-(trifluoromethyl)-2-[(trifluoromethyl)dioxy]propyl trifluoromethyl ether (**12**) had ir (67% **1**, 33% **12**) 1338 m, 1308 vs, 1287 vs, 1255 vvs, 1230 vs, 1201 vs, 1187 s, 1143 s, 1112 s, 1063 m, 1029 m, 964 m, 921 m, 890 m, 861 m, 768 m, 739 m, 690 m, 678 m, 652 m, 639 m, 620 m, 531 cm^{-1} m; mass spectrum *m/e* (rel intensity, assignment) 317 (0.2, $C_5F_{11}O_3$), 229 (0.2, $C_4F_7O_3$), 213 (0.2, $C_4F_7O_2$), 201 (3.7, $C_3F_7O_2$), 197 (0.3, C_4F_7O), 185 (5.2, C_3F_7O), 147 (0.9, C_3F_5O), 135 (0.8, C_2F_5O), 119 (2.0, C_2F_5), 116 (0.7, C_2F_4O), 97 (12.0, C_2F_3O), 78 (0.8, C_2F_2O).[20]

Reaction of c-C_5F_8. A very high yield of the expected 1:1 addition product is obtained. Nmr shows nearly equal amounts of the cis and trans products. Both show coupling between the CF_3O and CF_3OO groups. *cis*-1,2,2,3,3,4,4,5-Octafluoro-5-[(trifluoromethyl)dioxy]cyclopentyl trifluoromethyl ether (**13**) and *trans*-1,2,2,3,3,4,4,5-octafluoro-5-[(trifluoromethyl)dioxy]cyclopentyl trifluoromethyl ether (**14**) has ir (52% **13**, 48% **14**) 1322 s, 1291 vs, 1251 vs, 1241 sh, 1222 s, 1199 s, 1157 s, 1009 s, 979 s, 924 m, 877 m, 861 sh, 850 m, 749 m, 666 m, 620 m, 609 m, 585 m, 544 m, 522 cm^{-1} sh; mass spectrum *m/e* (rel intensity, assignment) 294 (0.2, $C_6F_{10}O_2$), 266 (2.2, $C_5F_{10}O$), 197 (2.3, C_4F_7O), 169 (4.3, C_3F_7), 166 (1.6, C_3F_6O), 159 (1.2, C_4F_5O), 150 (1.8, C_3F_6), 135 (1.4, C_2F_5O), 131 (8.1, C_3F_5), 119 (8.2, C_2F_5), 109 (1.9, C_3F_3O), 100 (5.2, C_2F_4), 97 (1.8, C_2F_3O), 93 (1.1, C_3F_3), 78 (1.3, C_2F_2O).[19]

Reaction of c-C_5H_8. Several attempts to observe the reaction of c-C_5H_8 with CF_3OOCF_3 were made, all without successful isolation of the expected product, $CF_3OOC_5H_8OCF_3$. Instead, ring opening apparently occurred with formation of many carbonyl containing compounds. The reaction contained considerable residue, presumably polymeric, which was not characterized.

Reaction of C_4F_6. The reaction proceeds with extensive polymerization. We were unable to isolate the expected product $C_2(CF_3OO)_2(CF_3O)_2(CF_3)_2$. We did observe two products which could not be separated on our gc column, presumably because of the C═O functions contained. 1,1,1,4,4,4-Hexafluoro-2,3-butanedione mono[bis(trifluoromethyl) acetal] (**15**) and 1,1,1,4,4,4-hexafluoro-2,3-butanedione mono[(trifluoromethyl)(trifluoromethoxy) acetal] (**16**) had ir (50% **15**, 50% **16**) 1790 s, 1286 vs, 1251 vvs, 1211 vs, 1202 vs, 1189 vs, 1139 vs, 1107 vs, 1080 s, 1061 s, 994 m, 931 s, 885 m, 789 m, 760 m, 734 m, 708 m, 680 m, 657 m, 610 m, 584 m, 553 m, 541 m, 515 m, 451 cm^{-1} m.

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References and Notes

(1) Presented in part at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 19, 1973.
(2) For a preliminary report of this work, see F. A. Hohorst and D. D. DesMarteau, *Chem. Commun.*, 386 (1973).
(3) R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5628 (1957); W. P. Van Meter and G. H. Cady, *ibid.*, **82**, 6005 (1960); C. I. Merrill and G. H. Cady, *ibid.*, **85**, 909 (1963); G. Franz and F. Newmayr, *Inorg. Chem.*, **3**, 921 (1964).
(4) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).
(5) P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Amer. Chem. Soc.*, **93**, 3882 (1971).
(6) P. A. Bernstein and D. D. DesMarteau, *J. Fluorine Chem.*, **2**, 315 (1972–1973).
(7) D. D. DesMarteau, *Inorg. Chem.*, **11**, 193 (1972).
(8) C. T. Ratcliffe, C. V. Hardin, L. R. Anderson, and W. B. Fox, *J. Amer. Chem. Soc.*, **93**, 3886 (1971).
(9) F. A. Hohorst and D. D. DesMarteau, *Inorg. Chem.*, submitted for publication.
(10) F. A. Hohorst and D. D. DesMarteau, to be published.
(11) N. Walker and D. D. DesMarteau, to be published.
(12) F. A. Hohorst, D. D. DesMarteau, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Amer. Chem. Soc.*, **95**, 3866 (1973).
(13) P. D. Bartlett and T. G. Taylor, *J. Amer. Chem. Soc.*, **85**, 2407 (1963); P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).
(14) W. A. Pryor, "Introduction to Free Radical Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1966.
(15) D. D. DesMarteau, *Inorg. Chem.*, **9**, 2174 (1970).
(16) R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5625 (1957).
(17) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3966 (1948).
(18) D. E. Gould, L. R. Anderson, D. E. Young, and W. G. Fox, *J. Amer. Chem. Soc.*, **91**, 1310 (1969).
(19) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.*, **91**, 2902 (1969).
(20) Further details of this portion of the work may be found in the Ph.D. Dissertation of Frederick A. Hohorst, Northeastern University, Boston, Mass., 1974.
(21) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. I, D. F. Detar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.
(22) L. R. Anderson and W. B. Fox, *J. Amer. Chem. Soc.*, **89**, 4313 (1967).
(23) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).