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PHOTOCHEMICAL REACTIONS OF FLUOROXYPERFLUOROALKANES WITH PERFLUOROCYCLOOLEFINS*

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SUMMARY

Under photolysis perfluoro-t-butyl hypofluorite readily undergoes one-electron reduction at -20°C in the presence of perfluorocycloolefin, which functions as a fluoroxy fluorine atom acceptor, to yield bis(perfluoro-t-butyl)peroxide as the major product. The other products are the simple adducts $C_5F_9OC(CF_3)_3$ and $C_6F_{11}OC(CF_3)_3$ from the corresponding perfluorocycloolefins C_5F_8 and C_6F_{10}, the cleavage compounds of $(CF_3)_3COF$ (i.e., CF_3COCF_3 and CF_4), the corresponding perfluorocycloalkanes, C_5F_{10} and C_6F_{12}, a small amount of vicinal perfluorodi-t-butoxycycloalkanes, and a trace of the dimers and oligomers. The formation of the peroxide $(CF_3)_3COOC(CF_3)_3$ confirms the homolysis of the O-F bond in $(CF_3)_3COF$ under photolysis.

The photochemical reactions of CF_3OF and perfluorocycloolefins at -60°C give mainly the simple adducts $C_5F_9OCF_3$ and $C_6F_{10}OCF_3$ from the corresponding perfluorocycloolefins. The other products are perfluorocycloalkanes, dimers, and oligomers, but the peroxide CF_3OOCF_3 and perfluorodimethoxycycloalkanes are absent.

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This paper examines the differences between the products of reactions of primary and tertiary fluoroxyperfluoroalkanes with perfluorocycloolefins and discusses the mechanisms of these reactions.

INTRODUCTION

This research represents part of an investigation elucidating the nature of addition reactions of fluoroxy groups to unsaturated perfluorocarbon bonds. The objective is to study the dissociation of the covalent O-F bond by homolytic and heterolytic fissions. Recently we reported that neat $(CF_3)_3COF$ is easily added to hexafluoropropene at -60°C to form a simple adduct $n\text{-}C_3F_7OC(CF_3)_3$.[1] The n-perfluoropropyl adduct suggests the ionic mechanism, the heterolytic fission of the O-F bond. The unique structural orientation of the product, since it is contrary to the usual nucleophilic fluoride ion adducts (i.e., the perfluoroisopropyl derivatives),[2,3] suggests electrophilic addition involving fluoronium ion.[1,4]

Although reactions involving electrophilic addition are not common for perfluoroolefins, Miller and Freedman[5] reported the electrophilic addition of mercuric fluoride to hexafluoropropene in anhydrous hydrogen fluoride. Such an electrophilic addition mechanism is further supported by Aldrich and coworkers,[6] who reported that the addition of mercuric fluoride is limited to terminal perfluoroolefins (because of the increased polarity of the terminal double bond) and that nonterminal perfluoroolefins do not react.

This work was initiated to prepare simple adducts of tertiary fluoroxyperfluoroalkanes and nonterminal perfluoroolefins. It was soon found that

$(CF_3)_3COF$ readily decomposed into fragments in the presence of perfluorocyclopentene, while the primary fluoroxyperfluoroalkane (CF_3OF) added to perfluorocyclopentene (C_5F_8) to form a simple adduct ($C_5F_9OCF_3$) as previously reported by Porter and Cady.[7]

This paper describes the photochemical reactions of primary and tertiary fluoroxyperfluoroalkanes with perfluorocycloolefins.

RESULTS AND DISCUSSION

Under photolysis the reaction of $(CF_3)_3COF$ and perfluorocycloolefin (C_5F_8 or C_6F_{10}) at -20°C gives a mixture of products, which includes the peroxide $(CF_3)_3COOC(CF_3)_3$ as the major product and the simple adducts $C_5F_9OC(CF_3)_3$ or $C_6F_{11}OC(CF_3)_3$, cleavage compounds of $(CF_3)_3COF$ (i.e., CF_3COCF_3 and CF_4), perfluorocycloalkanes C_5F_{10} or C_6F_{12}, a small amount of the vicinal perfluorodi-t-butoxycycloalkanes $C_5F_8[OC(CF_3)_3]_2$ or $C_6F_{10}[OC(CF_3)_3]_2$, and a trace of dimers and oligomers. The yields of the peroxide, hexafluoroacetone, and tetrafluoromethane increase with an increase of $(CF_3)_3COF$, while an increase of perfluorocycloolefin increases the other products.

The proposed reaction sequence described below is shown to be consistent with the observed products from the photochemical reactions of $(CF_3)_3COF$ and perfluorocycloolefins. Some possible reaction paths are presented to correlate and explain the results.

Initiation

$$(CF_3)_3COF \xrightarrow{h\nu} (CF_3)_3CO\cdot + F\cdot \qquad (1)$$

Reaction (1) initiates a series of reactions in the presence of perfluorocycloolefin, which functions as a fluoroxy fluorine atom acceptor. Reaction (2) is at least partially responsible for the enhancement of homolysis of the O-F bond in $(CF_3)_3COF$.

$$C_5F_8 \text{ (or } C_6F_{10}) + (CF_3)_3COF \xrightarrow{h\nu} C_5F_9\cdot \text{ (or } C_6F_{11}\cdot) + (CF_3)_3CO\cdot \qquad (2)$$

A simple combination of the two radical products of reaction (2) accounts for the formation of the simple adduct, perfluoro-t-butoxycyclopentane $C_5F_9OC(CF_3)_3$ and perfluoro-t-butoxycyclohexane $C_6F_{11}OC(CF_3)_3$ (see Tables 1 to 4).

When reactions of $(CF_3)_3COF$ and perfluorocycloolefins were carried out at 0°C without irradiation, the unimolecular chain decomposition of $(CF_3)_3COF$ occurred. The rapid decomposition is initiated by fluoroxy fluorine atom abstraction from the molecule and is then followed by β-scission of perfluoro-t-butoxy radical.

Propagation and termination

$$(CF_3)_3CO\cdot \rightarrow (CF_3)_2CO + CF_3\cdot \qquad (3)$$

$$(CF_3)_3COF + CF_3\cdot \rightarrow CF_4 + (CF_3)_3CO\cdot \qquad (4)$$

The chain reactions (3) and (4) proceed at such a rapid rate that they become almost the sole reactions to account for the cleavage products (i.e., hexafluoroacetone and tetrafluoromethane).

When the same reaction was carried out under photolysis at -20°C, the lower temperature slowed the unimolecular chain decomposition of $(CF_3)_3COF$. This rapid decomposition of the hypofluorite, which is not observed for

TABLE 1

^{19}F NMR SPECTRA OF SOME PERFLUOROCYCLOPENTYL ETHERS

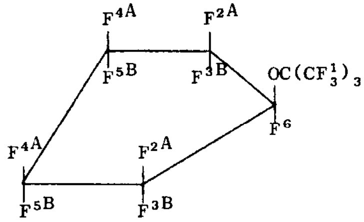
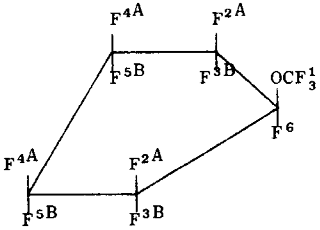
Compound	Relative Intensity	Chemical Shift φ (ppm from $CFCl_3$)	Coupling Constants J (Hz)	Assignment
	9	71.6	J(1,6)=14.9±0.2 J(1,2A)=3.2±0.2 J(1,3B)=3.2±0.2	1
		127.5		2A
	4		J(2A,3B)=258±3	
		131.3		3B
		134.3		4A
	4		J(4A,5B)=260±3	
		135.1		5B
	1	137.4	J(1,6)=14.9±0.2	6
	3	67.6	J(1,6)=10.0±0.2 J(1,2A)=6.0±0.2 J(1,3B)=4.6±0.2	1
		126.8		2A
	4		J(2A,3B)=260±3	
		137.1		3B
		131.8		4A
	4		J(4A,5B)=260±3	
		135.3		5B
	1	140.7	Complex multiplet	6

TABLE 1 (concluded)

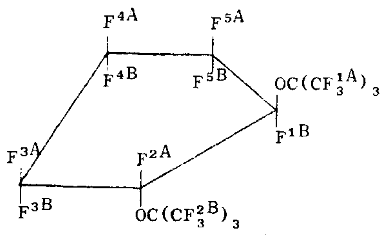
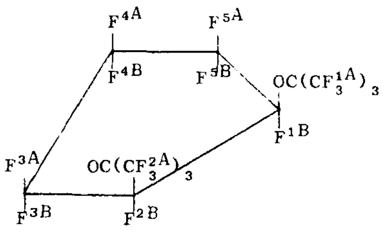
Compound	Relative Intensity	Chemical Shift φ (ppm from $CFCl_3$)	Coupling Constants J Hz	Assignment
	18	70.9		1A, 2B
	2	138.2	Broad	2A, 1B
		128.2		3A, 5B
	4		J(3A,5B)=J(5A,3B)= 250±3	
		127.6		5A, 3B
	2	130.4		4A, 4B
	18	71.1		1A, 2A
	2	135.7	Broad	1B, 2B
		130.1		3B, 5B
	4		J(3A,3B)=J(5A,5B)= 260±3	
		125.3		3A, 5A
		133.5		4B
	2		J(4A,4B)=260±3	
		129.3		4A

TABLE 2

MASS SPECTRA (LKB 9000) OF SOME PERFLUOROCYCLOPENTYL ETHERS AND DERIVATIVES

$C_5F_9OC(CF_3)_3$:	466 $C_9F_{18}O^+$ (0.0), 447 $C_9F_{17}O^+$ (3.9), 409 $C_9F_{15}O^+$ (0.5), 347 $C_7F_{13}O^+$ (4.1), 316 $C_6F_{12}O^+$ (3.6), 285 $C_5F_{11}O^+$ (2.3), 231 $C_5F_9O^+$ (6.0), 219 $C_4F_9^+$ (2.3), 212 $C_5F_8^+$ (1.1), 181 $C_4F_7^+$ (6.0), 147 $C_3F_5O^+$ (9.0), 131 $C_3F_5^+$ (8.0), 119 $C_2F_5^+$ (4.0), 100 $C_2F_4^+$ (4.0), 97 $C_2F_3O^+$ (15.0), 93 $C_3F_3^+$ (5.0), 69 CF_3^+ (100.0), 50 CF_2^+ (3.0), 31 CF^+ (3.0).
$C_5F_8[OC(CF_3)_3]_2$:	682 $C_{13}F_{26}O_2^+$ (0.3), 663 $C_{12}F_{25}O_2^+$ (9.6), 563 $C_{11}F_{21}O_2^+$ (8.3), 447 $C_9F_{17}O^+$ (0.7), 435 $C_8F_{17}O^+$ (3.3), 347 $C_7F_{13}O^+$ (20.0), 285 $C_5F_{11}O^+$ (1.0), 231 $C_5F_9^+$ (0.7), 219 $C_4F_9^+$ (6.0), 181 $C_4F_7^+$ (2.0), 169 $C_3F_7^+$ (1.7), 162 $C_4F_6^+$ (1.0), 150 $C_3F_6^+$ (0.7), 147 $C_3F_5O^+$ (2.3), 131 $C_3F_3^+$ (33.0), 119 $C_2F_5^+$ (1.7), 112 $C_3F_4^+$ (1.0), 109 $C_3F_3O^+$ (1.0), 100 $C_2F_4^+$ (4.3), 97 $C_2F_3O^+$ (5.3), 93 $C_3F_3^+$ (1.7), 69 CF_3^+ (100), 50 CF_2^+ (1.0), 47 CFO^+ (1.3), 31 CF^+ (1.3), 28 CO^+ or N_2^+ (1.3).
$C_5F_9OCF_3$:	316 $C_6F_{12}O^+$ (0.0), 297 $C_6F_{11}O^+$ (7.0), 231 $C_5F_9^+$ (75), 212 $C_5F_8^+$ (2.0), 209 $C_5F_7O^+$ (5.0), 193 $C_5F_7^+$ (3.0), 185 $C_3F_7O^+$ (2.0), 181 $C_4F_7^+$ (54), 162 $C_4F_6^+$ (5.0), 143 $C_4F_5^+$ (2.0), 131 $C_3F_5^+$ (100), 119 $C_2F_5^+$ (2.0), 100 $C_2F_4^+$ (14), 93 $C_3F_3^+$ (6.0), 69 CF_3^+ (26), 32 O_2^+ (8.0), 28 CO^+ or N_2^+ (36).
$[C_5F_8OCF_3]_2$:	594 $C_{12}F_{22}O_2^+$ (14), 506 $C_{11}F_{18}O_2^+$ (4), 444 $C_9F_{16}O_2^+$ (6), 421 $C_{10}F_{15}O^+$ (10), 409 $C_9F_{15}O^+$ (12), 393 $C_9F_{15}O_2^+$ (9), 378 $C_8F_{14}O^+$ (3), 343 $C_8F_{13}^+$ (4), 293 $C_7F_{11}^+$ (12), 262 $C_6F_{10}^+$ (2), 243 $C_6F_9^+$ (11), 221 $C_6F_7O^+$ (4), 193 $C_5F_7^+$ (10), 181 $C_4F_7^+$ (4), 162 $C_4F_6^+$ (3), 159 $C_4F_5O^+$ (2), 155 $C_5F_5^+$ (2), 143 $C_4F_5^+$ (7), 135 $C_2F_5O^+$ (7), 131 $C_3F_5^+$ (99), 119 $C_2F_5^+$ (6), 109 $C_3F_3O^+$ (6), 100 $C_2F_4^+$ (47), 69 CF_3^+ (100), 47 CFO^+ (4), 32 O_2^+ (4), 31 CF^+ (5), 28 CO^+ or N_2^+ (15).
$[C_5F_9]_2$:	462 $C_{10}F_{18}^+$ (0.0), 443 $C_{10}F_{17}^+$ (15), 393 $C_9F_{15}^+$ (5), 343 $C_8F_{13}^+$ (56), 293 $C_7F_{11}^+$ (10), 243 $C_6F_9^+$ (14), 205 $C_6F_7^+$ (4), 193 $C_5F_7^+$ (12), 181 $C_4F_7^+$ (6), 169 $C_3F_7^+$ (5), 162 $C_4F_6^+$ (4), 155 $C_5F_5^+$ (5), 143 $C_4F_5^+$ (10), 131 $C_3F_5^+$ (91), 119 $C_2F_5^+$ (12), 100 $C_2F_4^+$ (57), 93 $C_3F_3^+$ (13), 69 CF_3^+ (100), 31 CF^+ (4).

TABLE 3

^{19}F NMR SPECTRA OF SOME PERFLUOROCYCLOHEXYL ETHERS

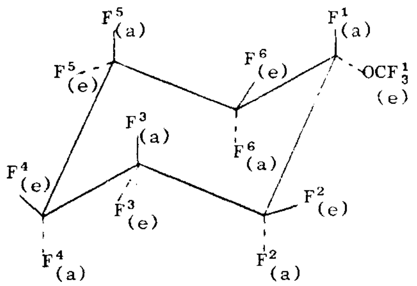
Compound	Relative Intensity	Chemical Shift φ (ppm from CFCl$_3$)	Coupling Constants J Hz	Assignment
	3	67.8		1(e)
	1	142.2		1(a)
	2	123.5		2(a), 6(a)
			J(2a,2e),J(6a,6e)=310±5	
	2	135.3		2(e), 6(e)
	2	125.9		3(a), 5(a)
			J(3a,3e),J(5a,5e)=295±5	
	2	137.8		3(e), 5(e)
	1	127.0		4(a)
			J(4a,4e)=305±5	
	1	138.7		4(e)

TABLE 3 (concluded)

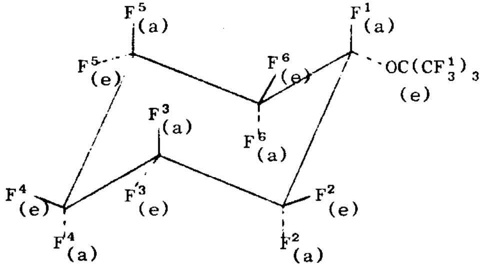
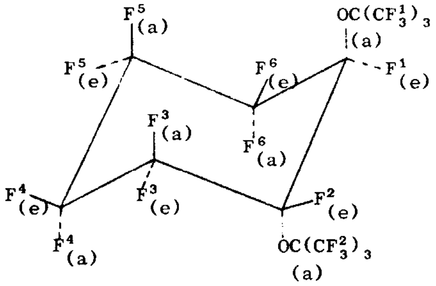
Compound	Relative Intensity	Chemical Shift φ (ppm from $CFCl_3$)	Coupling Constants J Hz	Assignment
	9	70.6	12±1	1e
	1	135.4		1a
	1	112.8		2a
			J(2a,2e)=300±5	
	1	116.8		2e
	1	116.9		6a
			J(6a,6e)=260±5	
	1	122.1		6e
	1	128.0		3a
			J(3a,3e)=260±5	
	1	132.6		3e
	1	138.6		5a
			J(5a,5e)=270±5	
	1	144.3		5e
	1	151.3		4a
			J(4a,4e)=300±5	
	1	155.5		4e
	18	70.7	7±1	1a, 2a
	2	139.6		1e, 2e
	2	126.2		3a, 6a
			J(3a,3e),J(6a,6e)=300±5	
	2	132.5		3e, 6e
	2	129.7		4a, 5a
			J(4a,4e),J(5a,5e)=300±5	
	2	135.3		4e, 5e

TABLE 4

MASS SPECTRA (LKB 9000) OF SOME PERFLUOROCYCLOHEXYL ETHERS

$C_6F_{11}OC(CF_3)_3$:	516 $C_{10}F_{20}O^+$ (0.0), 497 $C_{10}F_{19}O^+$ (4.5), 478 $C_{10}F_{18}O^+$ (0.6), 459 $C_{10}F_{17}O^+$ (1.6), 428 $C_9F_{16}O^+$ (1.3), 409 $C_9F_{15}O^+$ (9.3), 347 $C_7F_{13}O^+$ (2.5), 285 $C_5F_{11}O^+$ (3.1), 281 $C_6F_{11}^+$ (5.0), 231 $C_5F_9^+$ (5.3), 219 $C_4F_9^+$ (4.3), 193 $C_5F_7^+$ (2.0), 181 $C_4F_7^+$ (10.0), 169 $C_3F_7^+$ (0.6), 162 $C_4F_6^+$ (3.1), 150 $C_3F_6^+$ (0.6), 147 $C_3F_5O^+$ (3.1), 131 $C_3F_5^+$ (100.0), 119 $C_2F_5^+$ (4.4), 100 $C_2F_4^+$ (4.4), 97 $C_2F_3O^+$ (4.4), 93 $C_3F_3^+$ (3.8), 69 CF_3^+ (62.5), 28 CO^+ or N_2^+ (1.3).
$C_6F_{10}[OC(CF_3)_3]_2$:	732 $C_{14}F_{28}O_2^+$ (0.2), 713 $C_{14}F_{27}O_2^+$ (18.2), 694 $C_{14}F_{26}O_2^+$ (0.4), 675 $C_{15}F_{25}O_2^+$ (3.0), 551 $C_{10}F_{21}O_2^+$ (0.6), 532 $C_{10}F_{20}O_2^+$ (0.2), 513 $C_{10}F_{19}O_2^+$ (0.2), 497 $C_{10}F_{19}O^+$ (0.6), 485 $C_9F_{19}O^+$ (4.2), 459 $C_{10}F_{17}O^+$ (1.2), 447 $C_9F_{17}O^+$ (0.8), 409 $C_9F_{15}O^+$ (1.2), 397 $C_8F_{15}O^+$ (1.4), 378 $C_8F_{14}O^+$ (0.4), 347 $C_7F_{13}O^+$ (14.2), 285 $C_5F_{11}O^+$ (4.2), 237 $C_6F_7O_2^+$ (0.8), 231 $C_5F_9^+$ (1.2), 219 $C_4F_9^+$ (8.8), 200 $C_4F_8^+$ (1.2), 193 $C_5F_7^+$ (2.0), 181 $C_4F_7^+$ (5.0), 162 $C_4F_6^+$ (3.2), 159 $C_4F_5O^+$ (2.4), 150 $C_3F_6^+$ (1.2), 131 $C_3F_5^+$ (32.0), 119 $C_2F_5^+$ (2.4), 112 $C_3F_4^+$ (1.2), 109 $C_3F_3O^+$ (1.4), 100 $C_2F_4^+$ (2.6), 97 $C_2F_3O^+$ (2.8), 93 $C_3F_3^+$ (2.4), 69 CF_3^+ (100.0), 47 CFO^+ (2.0), 31 CF^+ (1.4).

CF_3OF in the presence of perfluorocycloolefins, confirms the stability of perfluoroalkoxy radicals in the following order:

$$CF_3O\cdot \;>\; (CF_3)_3CO\cdot$$

which agrees with the protonated analog.[8,9]

Reaction (5) accounts for the formation of perfluorocycloalkanes (C_5F_{10} and C_6F_{12}) and reaction (6) for the dimer of perfluorocycloalkanes.

$$F\cdot + C_5F_9\cdot \text{ (or } C_5F_{11}\cdot) \rightarrow C_5F_{10} \text{ (or } C_6F_{12}) \qquad (5)$$

$$2C_5F_9\cdot \text{ (or } 2C_6F_{11}\cdot) \rightarrow (C_5F_9)_2 \text{ (or } (C_6F_{11})_2) \qquad (6)$$

Reaction (7) must occur to some extent to give radicals $(CF_3)_3COC_5F_8\cdot$ or $(CF_3)_3COC_6F_{10}\cdot$,

$$(CF_3)_3CO\cdot + C_5F_8 \text{ (or } C_6F_{10}) \rightarrow (CF_3)_3COC_5F_8\cdot \text{ (or } (CF_3)_3COC_6F_{10}\cdot) \qquad (7)$$

which cross combine with perfluoro-t-butoxy radicals to form the small amount of vicinal perfluorodi-t-butoxycyclopentane $C_5F_8[OC(CF_3)_3]_2$ or vicinal perfluorodi-t-butoxycyclohexane $C_6F_{11}[OC(CF_3)_3]_2$.

$$(CF_3)_3CO\cdot + (CF_3)_3COC_5F_8\cdot \text{ (or } (CF_3)_3COC_6F_{10}\cdot) \rightarrow C_5F_8[OC(CF_3)_3]_2 \text{ (or } C_6F_{10}[OC(CF_3)_3]_2) \qquad (8)$$

The autocombination of perfluoro-t-butoxy radicals (Reaction 9) explains the formation of the main product, bis(perfluoro-t-butyl)peroxide.

$$2(CF_3)_3CO\cdot \rightarrow (CF_3)_3COOC(CF_3)_3 \qquad (9)$$

Thus the product formation of Reaction (8) can alternatively be expressed as follows:

$$(CF_3)_3COOC(CF_3)_3 + C_5F_8 \text{ (or } C_6F_{10}) \xrightarrow{h\nu} C_5F_8[OC(CF_3)_3]_2 \text{ (or } C_6F_{10}[OC(CF_3)_3]_2) \quad (10)$$

The photochemical reactions of primary fluoroxyperfluoroalkane (CF_3OF) and perfluorocycloolefins (C_5F_8 and C_6F_{10}) form mainly the simple adducts without forming bis(trifluoromethyl)peroxide or perfluorodimethoxycycloalkanes. The difference between the main reaction products of primary and of tertiary fluoroxyperfluoroalkanes can be explained by the shorter life-expectancy of trifluoromethoxy radical compared with perfluoro-t-butoxy radical because of the increased bulky groups surrounding the radical center. The longer·lifetime of the perfluoro-t-butoxy radicals enables them to autocombine (Reaction 9), and the absence of CF_3OOCF_3 and perfluorodimethoxycycloalkanes is directly related to the low concentration of $CF_3O\cdot$ radicals. Since the rate of dimerization of alkoxy radicals to form the peroxide is dependent on $[RO\cdot]^2$ due to the second-order reaction,[8] the low concentration of $CF_3O\cdot$ radicals greatly decreases the CF_3OOCF_3 formation. Consequently, no perfluorodimethoxycycloalkanes are detected as in Reaction (10).

For vicinal perfluorodi-t-butoxycyclopentane, the presence of cis- and trans-isomers in a 1:4 ratio is attributed to the involvement of free radical addition mechanisms (Reactions 7 and 8 or 10). The lack of stereospecificity excludes the involvement of tight ion pairs[10] or a four-centered addition mechanism. The trans-addition is favored as a result of steric repulsion caused by the two bulky perfluoro-t-butoxy groups at the vicinal cis-position.

More complex ^{19}F NMR spectra were obtained for perfluorocyclohexyl ethers (Table 3) than for perfluorocyclopentyl ethers (Table 1).[11] Feeney and Sutcliffe reported that, due to the strain and energetic grounds, perfluorocyclohexane and its derivatives have the chair configurations.[12] The bulky CF_3 group of perfluoromethylcyclohexane has been reported as fixed in the equatorial position.[12,13] Table 3 shows the ^{19}F NMR of perfluoromethoxy- and -t-butoxy groups at equatorial positions. Although the coupling constants and chemical shifts of perfluoromethoxy- and -methylcyclohexanes[13] are similar, perfluoro-t-butoxycyclohexane is more complex. This complexity is attributed to some rotational barriers[14,15] caused by the bulky perfluoro-t-butoxy group. The presence of only one isomer for vicinal perfluorodi-t-butoxycyclohexane is deduced from ^{19}F NMR (Table 3) as the 1,2-diaxial isomer.

EXPERIMENTAL

Reagents

Perfluoro-t-butyl hypofluorite was prepared by direct fluorination of the sodium salt of perfluoro-t-butanol at -23°C.[1] The liquid product was confirmed by infrared and ^{19}F NMR spectra as described by Prager and Thompson[16] for $(CF_3)_3COF$.

Perfluoro-t-butanol, trifluoromethyl hypofluorite, perfluorocyclopentene, and perfluorocyclohexene were obtained from PCR. These reagents were checked by infrared and ^{19}F NMR spectra and were freed from noncondensible impurities before use by condensation and pumping under vacuum in a trap cooled by liquid nitrogen.

Apparatus

All compounds were handled in quartz reaction vessels attached to a copper vacuum manifold system equipped with Monel valves and Cajon Ultratorr fittings. Pressures were measured by Ashcroft gauges to 75 psia and by a Pennwalt Wallace and Tiernan gauge (0-1550 mm Hg with an accuracy to 0.15 mm Hg). Amounts of volatile reactants were determined by P-V-T measurements, assuming ideal gas behavior.

The IR spectra were measured on a Perkin Elmer 467 spectrometer with a 5-cm Monel gas cell equipped with AgCl windows. The ^{19}F NMR spectra were determined with a Varian XL-100 spectrometer operating at 94.1 Hz, using $CFCl_3$ as an external reference at 30°C. Mass spectra were obtained from an LKB 9000 mass spectrometer, which has an ionizing potential of 70 eV and a resolving power of 2000. The gas chromatograph-mass spectra were also run on the LKB 9000 instrument, using a 3 m x 2 mm glass column packed with 1% SE 30 on Gas-Chrom Q at 30° to 80°C and 3 atm nitrogen pressure. The elemental analyses were obtained by a high resolution mass spectrometer (CEC 21-110-B). The molecular weights or parent ions were also determined by a field ionization mass spectrometer.

Reactions of Perfluoro-t-butyl Hypofluorite

(a) With perfluorocyclopentene

Perfluorocyclopentene (2.4 mmol, 0.51 g) was condensed onto an evacuated frozen perfluoro-t-butyl hypofluorite (4.7 mmol, 1.19 g) in a quartz reaction vessel at a temperature of -196°C. The solid mixture was then warmed to -20°C and irradiated by a high pressure Hg arc lamp with a focused beam for 1 hr at -20°C. The liquid was chilled to -40°C and evacuated. The volatiles (0.33 g, 19% yield) collected in a liquid nitrogen trap were identified by IR spectra as mainly CF_3COCF_3 and CF_4 with characteristic absorptions at 1890 and 2200 cm^{-1}, respectively. In addition small amounts of perfluorocyclopentane and perfluorocyclopentene were found with characteristic absorptions at 546 and 1776 cm^{-1}, respectively.

The residual mixture could not be cleanly separated by trap-to-trap distillation and was identified by ^{19}F NMR spectroscopy as $C_5F_9OC(CF_3)_3$ (Table 1, 0.85 mmol, 0.4 g) and the peroxide $(CF_3)_3COOC(CF_3)_3$ (1.3 mmol, 0.6 g). The ^{19}F NMR of the latter compound shows a single resonance at 69.7 ppm relative to $CFCl_3$ as the external reference.

The liquid mixture was further analyzed by a gas chromatograph-mass spectrograph using a 3 m x 2 mm glass column packed with 1% SE-30 on Gas-Chrom Q at 50°C with 3 atm nitrogen carrier gas pressure. Table 2 shows the mass spectra (LKB 9000) of $C_5F_9OC(CF_3)_3$ and $C_5F_8[OC(CF_3)_3]_2$. At higher gas chromatograph temperature (80°C), the mass spectrum showed a trace of oligomers.

The field ionization mass spectrum exhibited two peaks. The strong peak was at mass m/e value of 470, which corresponds to the parent ion or molecular weight of $(CF_3)_3COOC(CF_3)_3$. The other peak was at mass m/e value of 466, which corresponds to the parent ion or molecular weight of $C_5F_9OC(CF_3)_3$.

The characteristic IR absorptions of $C_5F_9OC(CF_3)_3$ are at 1300 cm^{-1} (s), 1290 cm^{-1} (s), 1276 cm^{-1} (s), 1235 cm^{-1} (s), 1180 cm^{-1} (m), 1130 cm^{-1} (m), 1065 cm^{-1} (w), 1004 cm^{-1}(s), 980 cm^{-1} (s), 600 cm^{-1} (w). Those of the peroxide $(CF_3)_3COOC(CF_3)_3$ are in accord with the literature.[17]

Mass spectroscopic molecular weight (CEC 21-110-B) of $C_5F_9OC(CF_3)_3$: Found 446.9685. Calculated for $C_9F_{17}O$ 446.9678. Mass spectroscopic molecular weight (CEC 21-110-B) of $C_5F_8[OC(CF_3)_3]_2$: Found, 681.9477. Calculated for $C_{13}F_{26}O_2$, 681.9483.

(b) With perfluorocyclohexene

Perfluorocyclohexene (2.0 mmol, 0.52 g) was condensed onto perfluoro-t-butyl hypofluorite (3.9 mmol, 0.99 g) and irradiated in the same manner as described above. The volatiles (0.35 g, 23% yield) were mainly CF_3COCF_3 and CF_4 in the presence of small amounts of perfluorocyclohexane and perfluorocyclohexene. The residual mixture, as deduced from ^{19}F NMR, contained the peroxide $(CF_3)_3COOC(CF_3)_3$ (1.3 mmol, 0.6 g) and the simple adduct $C_6F_{11}OC(CF_3)_3$ (0.4 mmol, 0.2 g, Table 3) as the major products. The mixture was further analyzed by gas chromatograph-mass spectra. Table [illegible] a trace of oligomers.

When the stoichiometry was changed to an excess of perfluorocyclohexene (2.46 g, 9.4 mmol) over perfluoro-t-butyl hypofluorite (0.79 g 3.1 mmol), the amount of volatiles (i.e., CF_3COCF_3 and CF_4) was decreased (0.29 g, 9% yield). The peroxide (0.87 mmol, 0.41 g) was also decreased, while the perfluorocyclohexyl ethers and oligomers were increased.

Reactions of trifluoromethyl hypofluorite

(a) With perfluorocyclopentene

Perfluorocyclopentene (4.0 mmol, 0.848 g) and trifluoromethyl hypofluorite (8.0 mmol, 0.864 g) were irradiated at -60°C for 1 hr and evacuated at -85°C. The volatile fraction was identified by IR spectrum as pure CF_3OF (3.8 mmol, 0.395 g).

The residual mixture was identified by ^{19}F NMR spectroscopy (Table 1) as $C_5F_9OCF_3$ (3.3 mmol, 1.04 g), C_5F_{10} (0.3 mmol, 0.075 g), the dimer of the simple adduct $(C_5F_8OCF_3)_2$ (0.13 mmol), and the dimer of perfluorocyclopentane $(C_5F_9)_2$ (0.02 mmol). The liquid mixture was further analyzed by a gas chromatograph-mass spectrograph, using the same column as described above but at 30°C with 3 atm nitrogen carrier gas pressure. Table 2 shows the mass spectra (LKB 9000) of $C_5F_9OCF_3$ and the dimers of the simple adduct $(C_5F_8OCF_3)_2$ and perfluorocyclopentane $(C_5F_9)_2$.

Mass spectroscopic molecular weight (CEC 21-110-B) of $(C_5F_8OCF_3)_2$ Found, 593,9547. Calculated for $C_{12}F_{22}O_2$, 593.9547. Mass spectroscopic molecular weight (CEC 21-110-B) for $(C_5F_9)_2$ is exactly the same as for $C_{10}F_{17}$.

(b) With perfluorocyclohexane

The reaction of perfluorocyclohexene (4.0 mmol, 1.05 g) and trifluoromethyl hypofluorite (8.0 mmol) was carried out in the same manner as the above procedure for CF_3OF and C_5F_8. The volatile fraction was identified by IR as pure CF_3OF, and the residual liquid was identified by ^{19}F NMR as quantitative and pure $C_6F_{11}OCF_3$ (Table 3).

Mass spectroscopic molecular weight (CEC 21-110-B) of $C_6F_{11}OCF_3$: Found, 346.9749. Calculated for $C_7F_{13}O$, 346.9749.

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