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ELECTROPHILIC ADDITIONS INVOLVING FLUORONIUM IONS
II. THE ADDITION OF FLUOROXY GROUPS TO PERFLUOROAROMATIC COMPOUNDS

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Summary

The addition of fluoroxy groups to perfluoroaromatic compounds results in the formation of stable adducts. Thus, for the reaction of equimolar quantities of hexafluorobenzene and trifluoromethyl hypofluorite, the main products are the 1,4-monofluoroxy and 1,2-monofluoroxy adducts, but the latter adduct is not detected in the corresponding reaction with perfluoro-t-butyl hypofluorite. Polyfluoroxy additions to perfluoroaromatic compounds occur more readily for $(CF_3)_3COF$ than for CF_3OF in spite of steric hindrance in the former. The other OF-containing compound which has been studied is oxygen difluoride which reacts with hexafluorobenzene to form polymeric perfluoroalicyclic ethers. In contrast to nucleophilic reactions, fluoroxy addition reactions occur more readily with hexafluorobenzene than with octafluorotoluene, a result which may be attributed to deactivation of the fluoroaromatic ring towards electrophilic addition by the trifluoromethyl group.

Introduction

The addition reactions between compounds containing fluoroxy groups and perfluoro-α-olefins result in the formation of interesting adducts which exhibit different orientations from the usual products of nucleophilic addition reactions [1, 2]. Recent nearly quantitative results relating to the electrophilic addition reactions between fluoroxyperfluoroalkane and hexafluoropropene [3] have prompted us to investigate the corresponding additions to perfluoroaromatic compounds [4]. Through such a study it would be possible to examine the attractive suggestion that these reactions are closely similar in that they exhibit the characteristic behaviour of electrophilic additions. In addition, such a study would provide further information regarding the involvement of fluoronium ions in these chemical reactions.

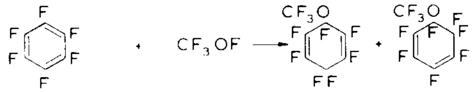
An earlier study showed that benzene reacted with trifluoromethyl hypofluorite to form fluorobenzene, a hypofluorite adduct being suggested as an unstable intermediate [5]. We now report the formation of stable hypofluorite adducts by addition of fluoroxy groups to perfluoroaromatics. Such addition reactions eliminate the probability of returning the dihydrobenzene derivative to the aromatic state. The existence of such stable adducts facilitates the investigation of the chemistry of fluoroxy additions at various positions in the nucleus of substituted perfluoroaromatics and enables a study of the effect of an initial adduct on subsequent addition reactions. From the preparative standpoint, addition of fluoroxy groups to perfluoroaromatics provides a convenient method for the synthesis of many new perfluoroalicyclic and polyalicyclic ethers.

Results and discussion

Much information has now been accumulated regarding the chemistry of perfluoroaromatic compounds. In a similar manner to perfluoro-olefins, their predominant feature is their susceptibility to nucleophilic attack [4, 5]. Thus, octafluorotoluene with an electron-withdrawing trifluoromethyl substituent provides a more activated ring system for nucleophilic reactions than hexafluorobenzene [6, 7]. In contrast, fluoroxyperfluoroalkanes add to hexafluorobenzene more readily than to octafluorotoluene, heating being required in the latter case before reaction occurs. This indicates that the electron-withdrawing trifluoromethyl group of octafluorotoluene deactivates the ring thus hindering electrophilic addition reactions.

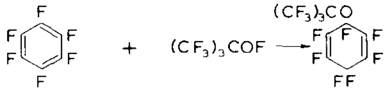
The number of fluoroxy groups which add to a perfluoroaromatic ring to form polyfluoroxy adducts may be increased by increasing the ratio of fluoroxy compounds to perfluoroaromatics present in the initial reaction mixture and also by utilizing the increased electrophilic character of $(CF_3)_3COF$ relative to CF_3OF. This increase in the electrophilicity of the tertiary fluoroxy compound relative to the primary is related to the strong inductive effect of perfluoroalkyl groups [8]. Thus Andreades [9] has shown that the rate of deuterium exchange increases by a factor of 10^9 for the following series of compounds in the order $CF_3H < C_6F_{13}CF_2H < (CF_3)_2CFH < (CF_3)_3CH$. The ease of multiple addition of fluoroxy groups to perfluoroaromatic compounds also increases from primary to tertiary hypofluorite, *i.e.* $CF_3OF < (CF_3)_3COF$, thus providing ready release of the fluoronium ion for electrophilic addition to the perfluoroaromatic ring. The greater steric requirements of the tertiary hypofluorite do not apparently inhibit polyaddition reactions.

Reaction of an equimolar quantity of hexafluorobenzene and trifluoromethyl hypofluorite resulted mainly in the formation of the 1,4- and 1,2-monofluoroxy adducts [(I) and (II)] in a 1:2 ratio.



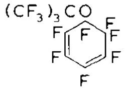
(I) (II)

When excess hexafluorobenzene was used in the reaction with perfluoro-t-butyl hypofluorite, the main product was the 1,4-monofluoroxy adduct (III).



(III)

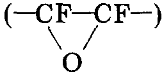
The 1,2 adduct (IV) was apparently not formed in this case.



(IV)

If the ratio of reactants employed was closer to equimolar, the two major products were found to be (III) (60% with respect to reacted hexafluorobenzene) and the difluoroxy adduct $C_6F_8[OC(CF_3)_3]_2$ (30%). The remaining higher molecular weight products (10%) were dimers of combined mono- and di-fluoroxy adducts $[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$, dimers of difluoroxy adducts and hexafluorobenzene $C_6F_7[OC(CF_3)_3]_2C_6F_5$, partially saturated dimers $C_6F_7[OC(CF_3)_3]_2C_6F_9$, a trace of trifluoroxy adduct $C_6F_9[OC(CF_3)_3]_3$ and a small amount of unidentified high molecular weight products.

The simplest difunctional fluoroxy-containing compound is oxygen difluoride. It reacts with hexafluorobenzene to form polyperfluoro-alicyclic ethers containing some internal epoxide (—CF—CF—) groups.



$$(-\underset{\diagdown\, O\, \diagup}{CF-CF}-)$$

Experimental

Reagents

Perfluoro-t-butyl hypofluorite (0.69 g) was prepared by direct fluorination of the sodium salt of perfluoro-t-butanol (0.70 g) at −23 °C [3]. The purity of the liquid product was confirmed from its IR and ^{19}F NMR spectra as described by Prager and Thompson [10] for $(CF_3)_3COF$.

Perfluoro-t-butanol and trifluoromethyl hypofluorite were obtained from PCR, Inc., and hexafluorobenzene and octafluorotoluene from Whittaker These reagents were checked by means of IR and ^{19}F NMR spectroscopic methods and were freed from non-condensible impurities before use by condensation and pumping under vacuum (0.1 mmHg) in a trap cooled with liquid nitrogen.

Apparatus

All compounds were handled in copper, stainless-steel, or Pyrex reaction vessels attached to a copper vacuum manifold system equipped with Monel valves and Cajon Ultratorr fittings. Pressures were measured by means of

Ashcroft gauges to 5 atm and by means of a Pennwalt Wallace and Tiernan gauge (0 - 1550 mmHg) which is accurate to 0.15 mmHg. 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. Liquid and solid samples were measured as thin films between AgCl windows. The ^{19}F NMR spectra were determined by means of a Varian XL-100 spectrometer operating at 94.1 MHz, using $CFCl_3$ as an external reference at 30 °C. Mass spectra were obtained using 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 × 2 mm glass column packed with 1% SE-30 on Gas-Chrom Q at 50 °C and *ca.* 1 atm nitrogen carrier gas pressure. Elemental analyses were obtained by means of a double-focusing high-resolution mass spectrometer (CEC 21-110-B).

*Reaction of trifluoromethyl hypofluorite with hexafluorobenzene**

An evacuated copper vacuum system was used to condense gaseous trifluoromethyl hypofluorite (19 mmol) on to evacuated frozen hexafluorobenzene (3.8 g, 20 mmol) at −196 °C. The frozen mixture was then warmed slowly to ambient temperature over a period of 1.5 h and to 40 °C over a further period of 1 h, and then evacuated at 0 °C. The volatile products were identified by IR spectroscopy and shown to consist mainly of bis(trifluoromethyl)peroxide and some hexafluorobenzene.

TABLE 1

Mass spectra of simple fluoroxy adducts of hexafluorobenzene and octafluorotoluene

$C_6F_7OCF_3$ [(I) and (II)]: 290 $C_7F_{10}O^+$ (2), 271 $C_7F_9O^+$ (21), 243 $C_6F_9^+$ (2), 205 $C_6F_7^+$ (53), 186 $C_6F_6^+$ (23), 183 $C_6F_5O^+$ (15), 155 $C_5F_4^+$ (23), 135 $C_2F_5O^+$ (3), 124 $C_4F_4^+$ (3), 117 $C_5F_7^+$ (18), 93 $C_3F_3^+$ (9), 69 CF_3^+ (100), 31 CF^+ (5).

$C_6F_7OC(CF_3)_3$ (III): 440 $C_{10}F_{16}O^+$ (3.6), 421 $C_{10}F_{15}O^+$ (85.7), 378 $C_8F_{14}O^+$ (3.6), 221 $C_6F_7O^+$ (4.3), 219 $C_4F_9^+$ (4.3), 205 $C_6F_7^+$ (100.0), 202 $C_6F_6O^+$ (10.7), 186 $C_6F_6^+$ (37.1),174 $C_5F_6^+$ (8.6), 159 $C_4F_5O^+$ (8.6), 155 $C_5F_5^+$ (28.6), 143 $C_4F_5^+$ (7.1), 131 $C_3F_5^+$ (10.7), 124 $C_4F_4^+$ (5.6), 117 $C_5F_3^+$ (12.1), 93 $C_3F_3^+$ (8.6), 69 CF_3^+ (64.2), 31 CF^+ (7.1).

$(CF_3)C_6F_6OCF_3$ (V): 340 $C_8F_{12}O^+$ (9.5), 321 $C_8F_{11}O^+$ (4.5), 274 $C_7F_{10}^+$ (11.2), 271 $C_7F_9O^+$ (3.0), 255 $C_7F_9^+$ (53.0), 233 $C_7F_7O^+$ (20.0), 224 $C_6F_8^+$ (18.0), 205 $C_6F_7^+$ (34.0), 155 C_5F_5 (27.0), 69 CF_3^+ (off scale).

$(CF_3)C_6F_8OCF_3$ (VI): 378 $C_8F_{14}O^+$ (0.8), 359 $C_8F_{13}O^+$ (1.0), 293 $C_7F_{11}^+$ (10.3), 278 $C_6F_9O^+$ (3.8), 262 $C_6F_{10}^+$ (1.0), 243 $C_6F_9^+$ (12.0).

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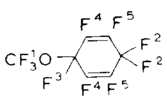
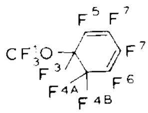
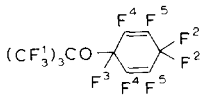
* **Caution.** The reactions of fluoroxy-containing compounds are potentially hazardous suitable protective equipment must be used when undertaking these reactions.

TABLE 2

NMR spectra of perfluoroalkyl heptafluorocyclohexadienyl ethers

Compound	Relative intensity	Chemical shift φ (ppm)	Coupling constant (Hz)	Assignment
 (I)	3	58.1		1
	1	125.5		3
	2	154.6		4
	2	157.7		5
	2	112.1		2
 (II)	3	57.4		1
	1	122.2		3
	2	112.9	J(A,B) = 300	4A, 4B
	1	147.0		5
	1	151.3		6
	2	155.3		7
 (III)	9	70.4		1
	1	118.1		3
	2	152.7		4
	2	157.4		5
	2	114.0		2

methyl)peroxide and some hexafluorobenzene. Evacuation at 0 °C was continued until the IR spectrum of the distillate showed complete absence of hexafluorobenzene. The vapor pressure of the residual clear liquid was *ca.* 10 mmHg at 25 °C.

Table 1 shows the mass spectrum of the liquid. This consists of trifluoromethyl heptafluorocyclohexadienyl ethers [(I) and (II)] as the major products together with some hexafluorobenzene and a trace amount of dimers containing the combined mono- and di-fluoroxy adducts, $(CF_3O)(C_6F_7)(C_6F_8)(OCF_3)_2$ (not included in Table 1). The precise structures of the primary products (I) and (II) were deduced from IR and ^{19}F NMR spectroscopic studies (Table 2), the 1:2 ratio of (I) to (II) being also deduced from the latter. The observed chemical shifts are of the same order as those reported for octafluorocyclohexadienes [11], and the value of 300 Hz for the coupling constant J(A,B) is similar to that for the related structures reported by Parsons [12]. The IR spectrum of the products exhibited a characteristic strong narrow absorption at 1748 cm^{-1} (C=C), a strong broad absorption in the 1370 - 1050 cm^{-1} region (C—F), and others at 1520 (m), 1000 (m), 890 (mw) and 710 (mw) cm^{-1}.

Reactions of perfluoro-t-butyl hypofluorite

With excess hexafluorobenzene

The reaction was carried out in an evacuated copper vacuum system. The neat liquid perfluoro-t-butyl hypofluorite (0.68 g, 2.72 mmol) was introduced slowly as a gas into the reaction vessel at 25 °C above excess liquid hexafluorobenzene (2.0 g, 10.8 mmol); the reaction vessel was then warmed to 40 °C. At first, the pressure decreased and then became nearly constant. The reaction vessel was cooled to —196 °C, allowed to warm slowly to 40 °C over a period of 15 min and then evacuated at 0 °C until the IR spectrum of the distillate showed the absence of hexafluorobenzene. The vapor pressure of the residual liquid was *ca.* 1 mmHg at 25 °C.

The IR spectrum of the liquid product exhibited characteristic absorptions at 1748 cm^{-1} (C=C) and in the 1370 - 1050 cm^{-1} region (C—F). The structure of the main product [(III)] was deduced from its ^{19}F NMR spectrum whose principal features are listed in Table 2. The mass spectrum of the liquid [given in Table 1 as (III)] indicates that it consists of perfluoro-t-butyl heptafluorocyclohexadienyl ether (III) as the main product in the presence of small amounts of hexafluorobenzene, the difluoroxy adduct $C_6F_8[OC(CF_3)_3]_2$ and dimers (which are not included in Table 1).

Mass spectroscopic molecular weight of (III): Found, 420.97095. Calculated for $C_{10}F_{15}O$, 420.97134.

With hexafluorobenzene

In this case, the reaction was undertaken using a mole ratio of reactants, perfluoro-t-butyl hypofluorite (2.0 g, 7.8 mmol) and hexafluorobenzene (1.7 g, 9.1 mmol), closer to 1:1. The process was varied by the intermittent addition of gaseous $(CF_3)_3COF$ at several increments to the total amount of C_6F_6 at 25 °C. After each addition, the reaction vessel was cooled to —196 °C and then warmed to 40 °C for 15 min. Finally, the reaction vessel was evacuated at —40 °C to enable the condensation of volatile products into a liquid nitrogen trap. These products (0.5 g) consisted of CF_3COCF_3, COF_2 and CF_4 as identified by their IR absorptions at 1890, 1950 and 2200 cm^{-1}, respectively.

The residual mixture was evacuated at 0 °C to enable a second fraction to be condensed into the nitrogen trap. This fraction (2.0 g) consisted of a clear liquid identified by ^{19}F NMR spectroscopy as a mixture of (III) (listed as such in Table 2; 1.4 g) and hexafluorobenzene [13] (φ 164.9, singlet; 0.6 g). The IR spectrum exhibited characteristic absorptions at 1748 cm^{-1} (C=C) and in the 1370 - 1050 cm^{-1} region (C—F). The mass spectrum of this second fraction is listed in Table 3 and indicates the presence of mainly (III) and C_6F_6, together with a small amount of the difluoroxy adduct, $C_6F_8[OC(CF_3)_3]_2$.

The third residual fraction was separated by decantation and consisted of (i) a liquid (0.9 g) and (ii) a solid fraction (0.3 g). The third (liquid) fraction consisted mainly of the difluoroxy adduct $C_6F_8[OC(CF_3)_3]_2$ and some (III). The mass spectral data listed in Table 3 show that the third (liquid) fraction exhibits a significant increase in relative abundance at *m/e* 675 (the parent difluoroxy adduct ion minus fluorine), absence of *m/e* 440 (the parent monofluoroxy adduct ion) and a further increase in relative abundance at

TABLE 3

Mass spectra of fractionation products

Second fraction[a]

$C_6F_8[OC(CF_3)_3]_2$, $C_6F_7OC(CF_3)_3$, C_6F_6: 694 $C_{14}F_{26}O_2^+$ (0.0), 675 $C_{14}F_{25}O_2^+$ (0.4), 478 $C_{10}F_{18}O^+$ (0.2), 475 $C_{10}F_{17}O_2^+$ (0.08), 459 $C_{10}F_{27}O^+$ (0.8), 440 $C_{10}F_{16}O^+$ (2.4), 421 $C_{10}F_{15}O^+$ (6.7), 378 $C_8F_{14}O^+$ (0.8), 285 $C_5F_{11}O^+$ (0.2), 243 $C_6F_9^+$ (1.6), 205 $C_6F_7^+$ (100.0), 202 $C_6F_6O^+$ (2.4), 193 $C_5F_7^+$ (6.4), 186 $C_6F_6^+$ (62.4).

Third (liquid) fraction[b]

$C_6F_8[OC(CF_3)_3]_2$: 694 $C_{14}F_{26}O_2^+$ (0.0), 675 $C_{14}F_{25}O_2^+$ (4.8), 459 $C_{10}F_{17}O^+$ (4.0), 421 $C_{10}F_{15}O^+$ (100.0), 221 $C_6F_7O^+$ (4.0), 219 $C_4F_9^+$ (4.0), 205 $C_6F_7^+$ (56.0), 202 $C_6F_6O^+$ (12.0), 193 $C_5F_7^+$ (12.0), 186 $C_6F_6^+$ ($\gg$ 100.0).

Third (solid) fraction

675 $C_{14}F_{25}O_2^+$ (7.0), 475 $C_{10}F_{17}O_2^+$ (1.6), 459 $C_{10}F_{17}O^+$ (8.0), 456 $C_{10}F_{16}O_2^+$ (0.8), 440 $C_{10}F_{16}O^+$ (0.8), 437 $C_{10}F_{15}O_2^+$ (0.8), 421 $C_{10}F_{15}O^+$ (100.0), 378 $C_8F_{14}O^+$ (3.2), 285 $C_5F_{11}O^+$ (2.4), 243 $C_6F_9^+$ (1.6), 221 $C_6F_7O^+$ (3.2), 219 $C_4F_9^+$ (4.0), 205 $C_6F_7^+$ (53.6), 202 $C_6F_6O^+$ (12.0), 153 $C_5F_7^+$ (12.0), 186 $C_6F_6^+$ ($>$ 100).

[a] Neat sample.

[b] C_6F_6 was added as a solvent to enable syringe injection of samples into the mass spectrometer.

m/e 421 and 205 in comparison to the second fraction. The ^{19}F NMR spectrum of this third (liquid) fraction shows the presence of a small amount of (III) (Table 2), the difluoroxy adducts being complex because of the presence of various isomers. The IR spectrum of the third (liquid) fraction exhibited an absorption at 1730 cm^{-1} (C=C) in agreement with the C=C absorption for the third (solid) fraction, but a shift from the absorption at 1748 cm^{-1} exhibited by the monofluoroxy adduct present in the second fraction.

The third (solid) fraction (0.3 g) has also been characterized by IR, ^{19}F NMR and gas chromatograph–mass spectra. The IR spectrum exhibited characteristic absorptions at 1730 cm^{-1}(C=C) and in the 1370 - 1050 cm^{-1} region (C—F). The ^{19}F NMR spectra were similar to those for the third (liquid) fraction but with the increased presence of additional peaks at φ 182 - 184 (bridgehead CF) and peaks at φ 164 - 165 corresponding to fluorines situated at C-3, C-4 and C-5 in monosubstituted hexafluorobenzene [13]. The solid mixture was dissolved in hexafluorobenzene and separated by passing through a 3 m × 2 mm glass column packed with 1% SE-30 on Gas-Chrom Q at 50 °C using *ca.* 1 atm nitrogen carrier gas pressure. The resulting gas chromatogram exhibited more than 30 peaks. The mass spectra of the major components of the 30 peaks arranged in order of increasing elution time are listed in Table 4. The various percentages of these major components (Table 4) were deduced from the relative peak areas of the gas chromatogram for the solid fraction.

TABLE 4

Mass spectra of the major components of the third (solid) fraction as separated by gas chromatography

$C_6F_8[OC(CF_3)_3]_2$ (4%)[a]: 694 $C_{14}F_{26}O_2^+$ (0.0), 675 $C_{14}F_{25}O_2^+$ (1.0), 475 $C_{10}F_{17}O_2^+$ (0.1), 459 $C_{10}F_{17}O^+$ (1.3), 420 $C_{10}F_{15}O^+$ (0.5).

$C_6F_9[OC(CF_3)_3]_3$ (1%)[a]: 948 $C_{18}F_{36}O_3^+$ (0.0), 891 $C_{18}F_{33}O_3^+$ (0.2), 691 $C_{14}F_{25}O_3^+$ (0.1), 675 $C_{14}F_{25}O_2^+$ (0.2), 421 $C_{10}F_{15}O^+$ (0.5).

$C_6F_9[OC(CF_3)_3]_2C_6F_5$[b] (9%)[a]: 880 $C_{20}F_{32}O_2^+$ (0.0), 675 $C_{14}F_{25}O_2^+$ (0.2), 645 $C_{14}F_{23}O^+$ (0.8), 626 $C_{16}F_{22}O^+$ (1.0), 607 $C_{16}F_{21}O^+$ (2.5), 459 $C_{10}F_{17}O^+$ (0.5), 421 $C_{10}F_{15}O^+$ (0.5).

$C_6F_7[OC(CF_3)_3]_2C_6F_5$[b] (9%)[a]: 842 $C_{20}F_{30}O_2^+$ (0.0), 675 $C_{14}F_{25}O_2^+$ (0.01), 623 $C_{16}F_{21}O_2^+$ (0.01), 607 $C_{16}F_{21}O^+$ (0.01), 421 $C_{10}F_{15}O^+$ (0.5).

$C_6F_9[C_6F_7]\,[OC(CF_3)_3]_2$ (9%)[a]: 918 $C_{20}F_{34}O_2^+$ (0.0), 899 $C_{20}F_{33}O_2^+$ (0.2), 880 $C_{20}F_{32}O_2^+$ (0.06), 861 $C_{20}F_{31}O_2^+$ (0.2), 823 $C_{20}F_{29}O_2^+$ (0.3), 675 $C_{14}F_{25}O_2^+$ (0.2), 588 $C_{16}F_{20}O^+$ (0.4), 459 $C_{10}F_{17}O^+$ (0.8), 421 $C_{10}F_{15}O^+$ (0.05).

$C_6F_9[C_6F_7][OC(CF_3)_3]_2$ (4%)[a]: 918 $C_{20}F_{34}O_2^+$ (0.0), 899 $C_{20}F_{33}O_2^+$ (0.2), 880 $C_{20}F_{32}O_2^+$ (2.0), 861 $C_{20}F_{31}O_2^+$ (9.5), 675 $C_{14}F_{25}O_2^+$ (0.5).

$C_6F_9[C_6F_7][OC(CF_3)_3]_2$ (2%)[a]: 918 $C_{20}F_{34}O_2^+$ (0.0), 899 $C_{20}F_{33}O_2^+$ (0.08), 880 $C_{20}F_{32}O_2^+$ (0.2), 861 $C_{20}F_{31}O_2^+$ (1.4), 675 $C_{14}F_{25}O_2^+$ (8.4).

$C_6F_9[C_6F_7][OC(CF_3)_3]_2$ (4%)[a]: 918 $C_{20}F_{34}O_2^+$ (0.0), 880 $C_{20}F_{32}O_2^+$ (2.0), 861 $C_{20}F_{31}O_2^+$ (8.5), 675 $C_{14}F_{25}O_2^+$ (5.0).

$[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$ (4%)[a]: 1134 $C_{24}F_{42}O_3^+$ (0.0), 1077 $C_{24}F_{39}O_3^+$ (0.04), 899 $C_{20}F_{33}O_2^+$ (0.02), 880 $C_{20}F_{32}O_2^+$ (0.08), 861 $C_{20}F_{31}O_2^+$ (0.76), 675 $C_{14}F_{25}O_2^+$ (1.1).

$[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$ (4%)[a]: 1134 $C_{24}F_{42}O_3^+$ (0.0), 1096 $C_{24}F_{40}O_3^+$ (2.0), 1077 $C_{24}F_{39}O_3^+$ (4.0), 877 $C_{20}F_{31}O_3^+$ (4.0), 861 $C_{20}F_{31}O_2^+$ (5.0), 823 $C_{20}F_{29}O_2^+$ (10.0).

$[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$ (13%)[a]: 1134 $C_{24}F_{42}O_3^+$ (0.0), 1077 $C_{24}F_{39}O_3^+$ (0.01), 861 $C_{20}F_{31}O_2^+$ (0.08), 823 $C_{20}F_{29}O_2^+$ (0.12).

$[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$ (9%)[a]: 1134 $C_{24}F_{42}O_3^+$ (0.0), 861 $C_{20}F_{31}O_2^+$ (0.01), 823 $C_{20}F_{29}O_2^+$ (0.08).

$[(CF_3)_3CO][C_6F_7][C_6F_8][OC(CF_3)_3]_2$ (2%)[a]: 1134 $C_{24}F_{42}O_3^+$ (0.0), 1115 $C_{24}F_{41}O_3^+$ (0.1), 1096 $C_{24}F_{40}O_3^+$ (0.25), 1077 $C_{24}F_{39}O_3^+$ (1.5), 675 $C_{14}F_{25}O_2^+$ (0.5).

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[a] The percent of the various compounds were deduced from the relative peak areas of the gas chromatogram. The compounds listed in the table are arranged in order of increasing elution time.

[b] The dimers contain the difluoroxy adduct portion $C_6F_7[OC(CF_3)_3]_2$, as deduced from the presence of *m/e* 675, and C_6F_5 as confirmed by ^{19}F NMR spectra which exhibited peaks at $\varphi = 164 - 165$ ppm.

Reaction of trifluoromethyl hypofluorite with octafluorotoluene

The same procedure as described above for trifluoromethyl hypofluorite with hexafluorobenzene was used for this reaction. In this case, however, no appreciable reaction occurred between an equal molar ratio (16 mmol) of octafluorotoluene and trifluoromethyl hypofluorite until the temperature was raised to 100 °C. After 8 h at 100 °C, the main by-product was bis(trifluoromethyl)peroxide as identified by its IR spectrum [14]. The vapor pressure of the residual liquid was *ca.* 4 mmHg at 25 °C.

The major product of the reaction was perfluoromethylmethoxycyclohexadiene (V) with perfluoromethylmethoxycyclohexene (VI) as a minor product together with a trace of the dimer arising from the two monofluoroxy adducts, *i.e.* $(CF_3)_2(C_6F_6)_2(OCF_3)_2$. No difluoroxy adducts of the type $(CF_3)(C_6F_6)(OCF_3)_2$ or dimers of the combined mono- and di-fluoroxy adducts, *i.e.* $(CF_3)_2(C_6F_6)_2(OCF_3)_3$, were detected by mass spectrometry. The mass spectra of (V) and (VI) are listed in Table 1. The ^{19}F NMR spectra were complex because of the presence of various isomers of the adducts. The absence of peaks at *ca.* φ 183 (bridgehead CF) [13] indicates that one C=C bond in the cyclic ring is attached to the trifluoromethyl substituent. The IR spectrum of the perfluoroether products exhibited two medium narrow characteristic absorption peaks at 1778 and 1719 cm^{-1} (C=C), a strong broad absorption in the 1370 - 1050 cm^{-1} region (C—F) and others at 1410 (m), 995 (s), 911 (mw), 855 (w) and 725 (w) cm^{-1}.

Reaction of oxygen difluoride with hexafluorobenzene

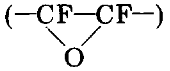
An evacuated copper vacuum manifold and a 12 cm^3 stainless-steel reaction vessel were used to condense OF_2(27.2 mmol) on to frozen hexafluorobenzene (7.9 mmol) at —196 °C; the reaction vessel was then warmed to —80 °C for 1 h. The OF_2 was vacuum-condensed into another container at —196 °C and warmed to 25 °C to check the pressure change as well as the composition of OF_2 (*via* its IR spectrum) in the container and the composition of the hexafluorobenzene remaining in the reaction vessel. The OF_2 was condensed back into the reaction vessel at —196 °C and then raised to a higher temperature. This process was repeated at —55 °C, —23 °C and 0 °C. No drop in the pressure of OF_2 or changes in composition were detected until the temperature reached 0 °C. After the volatile products had been condensed back into the reaction vessel, they were warmed back to 0 °C over a period of 40 h and then evacuated at —150 °C in order to remove unreacted OF_2 (7.23 mmol of the latter being consumed in the reaction). Evacuation was continued at 0 °C when a small quantity of volatile material was removed but no hexafluorobenzene. The residue (60% yield) was found to be polymeric. The IR spectrum of this product exhibited a very weak absorption at 1738 cm^{-1} (C=C) and a weak absorption at 1491.5 cm^{-1}  $(-\underset{\diagdown\,O\,\diagup}{\mathrm{CF}-\mathrm{CF}}-)$ [15], a strong broad absorption in the 1370 - 1100 cm^{-1} region (C—F) and

TABLE 5

NMR spectrum of polymeric adduct of OF_2 and hexafluorobenzene

Adduct	Relative intensity	Chemical shift φ (ppm)	Assignment
CF_3^1 or OCF_2^1	1	81	1
CF_2^2	36	126	2
OCF^3	10	155	3
CF^4	8	180	4

other strong absorptions in the 1070 - 970 cm^{-1} region. Data relating to the ^{19}F NMR spectrum of the residual polymer as a solution in hexafluorobenzene are listed in Table 5. The ^{19}F NMR and IR spectra indicate that the polymer contains mainly saturated perfluoroalicyclic ethers with some internal epoxide groups.

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