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ELECTROPHILIC ADDITIONS INVOLVING FLUORONIUM IONS. I. FLUOROXY ADDITIONS TO PERFLUORO-OLEFINIC BONDS

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Summary

The fluoroxy addition of perfluoro-t-butyl hypofluorite to hexafluoropropene leads predominantly (> 95%) to perfluoro-n-propyl perfluoro-t-butyl ether. The unique structural orientation of this perfluoro-n-propyl product is of interest because the products of fluoride ion addition reactions have previously been reported as perfluoroisopropyl derivatives. The results obtained in this study provide a simple experimental demonstration of electrophilic attack by the O—F group, leading to the addition of the fluoronium ion to the more nucleophilic unsaturated carbon atom.

The same mechanism as for a perfluoro-α-olefin applies in fluoroxy addition to a perfluorovinyl ether. The perfluoro-t-butoxy group also adds predominantly (> 95%) to the terminal unsaturated carbon atom.

Introduction

Organic reactions of fluoroxy compounds, particularly fluoroxy trifluoromethane (CF_3OF), have been extensively studied. Barton and coworkers discovered that CF_3OF, as a versatile electrophilic fluorinating agent which constitutes a source of "electrophilic fluorine", can selectively and rapidly effect the electrophilic fluorination of activated olefins [1]. Barton *et al.* also demonstrated the efficient consumption of CF_3OF by olefins in the presence of a large excess of radical-reacting compounds, and that the presence of radical "scavengers" had no effect on the number, nature, or proportion of the products. As a result, these authors precluded homolytic scission of the O—F bonds of fluoroxy compounds before attack on ethylenic linkages as well as the involvement of free radicals during the later stages of fluoroxy addition reactions [2].

The susceptibility of perfluoro-olefins to attack by anions or nucleophiles and their corresponding resistance to cation attack by anions been [3 - 5]. Because of the strong inductive effect of a perfluoroalkyl substituent [6,7] attached to a perfluoro-α-olefinic bond, the terminal difluoromethylene carbon is the more electrophilic terminus and hence the most open to nucleophilic attack.

In contrast to fluoroanionic addition reactions, addition of fluoroxy to hexafluoropropene leads to the n-perfluoropropyl derivative. Thus perfluoro-n-propyl perfluoro-t-butyl ether (II) was obtained in > 95% yield. This suggests that the reaction of hexafluoropropene and perfluoro-t-butyl hypofluorite (I) involves electrophilic attack by the O—F group and is therefore a fluoronium addition reaction.

$$\overset{\leftrightarrow\,\delta^-}{CF_3CF}=\overset{\delta^+}{CF_2} + F\overset{\frown}{-}OC(CF_3)_3 \rightarrow [CF_3CF_2CF_2^+\ {}^-OC(CF_3)_3] \rightarrow \underset{c\ \ d\ \ b\ \ \ a}{CF_3CF_2CF_2OC(CF_3)_3}$$

$$\underset{\delta^+\ \delta^-}{}$$

(I) (II)

Attempts to obtain a simple fluoroxy adduct of (I) and perfluorocyclopentene were unsuccessful despite reports that CF_3OF gives a simple adduct almost quantitatively [8], and this suggests that the stability of the perfluoro-t-butoxy anion relative to the trifluoromethoxy group may influence ring opening and the formation of fragmented products.

The perfluoro-t-butoxy group also adds predominantly (> 95%) to the unsaturated terminal carbon atom of perfluoro-3,6-dioxy-5-methyl-n-non-1-ene* (III) as a result of electrophilic attack of the O—F group of (I) to give perfluoro-2,2,8-trimethyl-3,6,9-trioxy-n-dodecane (IV).

$$CF_3CF_2CF_2OCF(CF_3)\overset{\leftrightarrow}{C}F_2OCF{=}CF_2 + (I) \rightarrow$$

(III)

$$\underset{i\ \ h\ \ g\ \ \ f\ \ e\ \ d\ \ \ c\ \ b\ \ \ a}{CF_3CF_2CF_2OCF(CF_3)CF_2OCF_2CF_2OC(CF_3)_3}$$

(IV)

Experimental**

Reagents

Hexafluoropropene, perfluoro-t-butanol and perfluoro-octane (90% n-C_3F_{18}) were obtained from PCR, Inc., $CFCl_3$ from du Pont, hexafluorobenzene from Whittaker and n-pentane from Mallinckrodt. These reagents were checked by infrared spectroscopy and the former two also by means of their ^{19}F NMR spectra. The 57% sodium hydride in mineral oil was used as received from Alpha Inorganics.

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* Perfluoro-3,6-dioxy-5-methyl-n-non-1-ene (b.p. 96 °C) was provided through the courtesy of Dr. C. Tamborski, Air Force Materials Laboratory, Wright–Patterson Air Force Base, Dayton, Ohio.

** The reactions of fluoroxy compounds are potentially hazardous, because of the high energy content and oxidizing reactivity of O—F bonds. Suitable protective equipment must be used when working with these reactions.

Instrumentation

Infrared spectra were recorded on a Perkin–Elmer 467 spectrometer using a 5 cm or 10 cm metal cell fitted with silver chloride windows. ^{19}F NMR spectra were recorded on a Varian XL-100 spectrometer at 94.1 MHz using trichlorofluoromethane and hexafluorobenzene as external references and with deuterated acetone as an external lock. The electron-impact mass spectra were determined by an LKB 9000 mass spectrometer, which has an ionizing potential of 70 eV and a resolving power of 2000. The elemental analyses were undertaken by means of a double-focusing, high-resolution mass spectrometer (CEC 21-110-B) and the molecular weight or parent ion was determined by a field ionization mass spectrometer.

Preparation of perfluoro-t-butyl hypofluorite (I)

The method described by Prager and Thompson [9] was found to be unsatisfactory as no reaction occurred when the direct fluorination of perfluoro-t-butanol was attempted at −20 °C. The following indirect route was thus used to prepare perfluoro-t-butyl hypofluorite *via* the direct fluorination of the sodium salt of perfluoro-t-butanol.

The mineral oil in the commercial sample of sodium hydride was replaced by n-pentane and the sample washed three times with n-pentane to ensure the complete removal of the mineral oil. The suspension of NaH in n-pentane was added dropwise to perfluoro-t-butanol at 0 °C until the evolution of hydrogen ceased. The resulting sodium alcoholate precipitated and settled at the bottom of the separating funnel. Saturated perfluorocarbon (90% n-C_8F_{18}) was then added to the funnel and stirred gently with a thin rod. The funnel was chilled by the use of powdered Dry Ice and this resulted in an improved separation at the interface between the two liquids (n-pentane and perfluoro-octane). The solid at the bottom and the bottom layer of suspended material in perfluoro-octane were separated and evacuated leaving a white solid residue.

A mixture of this residue (1.5 g, equivalent to 0.005 mol of $(CF_3)_3CONa$) and an equal amount by weight of NaF were placed on the glass frit in the fluorine-flow apparatus (Fig. 1). Fluorination was continued over a 3 h period at −23 °C (CCl_4 slush bath) using 0.02 mol of fluorine (passed as a 10% mixture in nitrogen at a total pressure of 50 mmHg). The volatile products were collected in a glass bead trap at −196 °C, the fluorine being separated by pumping through a liquid nitrogen trap followed by conversion to CF_4 in a charcoal scrubber preceding the pump. As a result of fluorination, the white sodium alcoholate powder was converted to sodium fluoride which remained on the glass frit. The volatiles collected in the glass bead trap were condensed on to a Pyrex finger as product (I) in almost quantitative yield. The IR spectrum of (I) agreed with that of purified $(CF_3)_3COF$ [9].

Preparation of perfluoro-n-propyl perfluoro-t-butyl ether (II)

The lowest convenient temperature for the slow fluoroxy addition

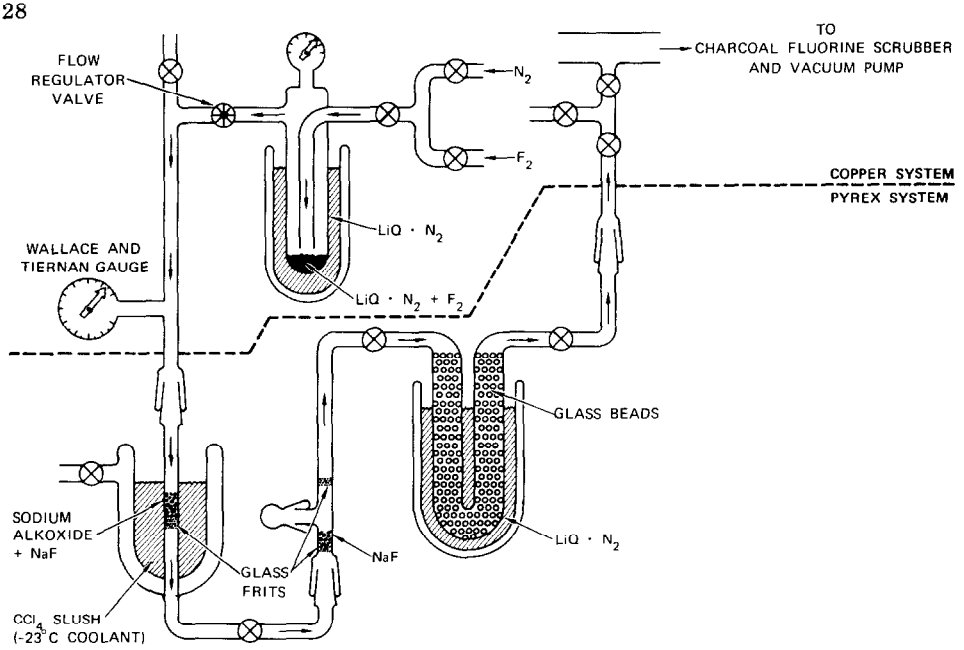

Fig. 1. Schematic diagram of fluorine-flow system.

reaction of (I) and hexafluoropropene was found to be −62 °C ($CHCl_3$ slush bath). No reaction occurred between (I) and gaseous hexafluoropropene at −80 °C when the former was held under the autogenous vapor pressure of the latter for 0.5 h. When the temperature was increased to −62 °C the initial rate of disappearance of hexafluoropropene was 5.6×10^{-2} mol s^{-1} at 100 mmHg pressure. Gaseous hexafluoropropene was added intermittently at *ca.* 100 mmHg pressure at −62 °C until the total pressure dropped to 50 mmHg. With the reactor and the hexafluoropropene reservoir both maintained at −62 °C, the valve between them was opened overnight and the contents allowed to warm gradually to room temperature over a period of 3 - 4 h. After removal of the excess perfluoropropene, the residual liquid was found to be the product (II) in almost quantitative yield with a vapor pressure of 25 mmHg at 25 °C. The isomeric impurity of (II) was less than 5%.

The IR spectrum of (II) exhibited no bands in the region between 2.5 μ and 7.2 μ, a strong absorption in the 7.3 - 9.1 μ region (C—F) and others at 9.9 (s), 10.1 (s), 12.3 (w), 13.3 (m), 13.5 (m) and 16.1 (w) μ. The ^{19}F NMR spectrum exhibited four peaks: δ 7.14 ppm [triplet, a, J(ab) = 9.15 Hz, relative peak area 9.3, 9F, $C(\underline{C}F_3)_3$], 82.0 ppm [multiplet, b, relative peak area 2.1, 2F, $C\underline{F}_2$], 83.0 ppm [triplet, c, J(bc) = 7.40 Hz, relative peak area 3.1, 3F, $C\underline{F}_3$] and 130.0 ppm [singlet, d, relative peak area 2.0, 2F, $C\underline{F}_2$]. The mass spectrum (LKB 9000) exhibited a highest mass m/e value of 385 (mass $C_7F_{16}O$ minus one fluorine atom). Mol. wt. (mass spectroscopy CEC 21-110-B): Found: 384.97247. $C_7F_{15}O$ requires 384.97075.

TABLE 1

The mass spectrum of product (IV)

Ion	Mass	Relative abundance
$C_{12}F_{26}O_3$ (parent ion, M)	686	0.0
$C_{12}F_{25}O_2$ (M—FO)	651	0.3
$C_{11}F_{22}O_3$ (M—CF_4)	598	0.4
$C_9F_{19}O_2$ (M—C_3F_7O)	501	1.4
$C_6F_{13}O$ (M—$C_6F_{13}O$)	335	35.9
$C_5F_{11}O$	285	7.7
C_4F_9 (perfluoro-t-butyl)	219	11.3
C_3F_7	169	87.3
C_3F_4O	140	2.5
$C_3F_3O_2$	137	3.0
C_3F_5	131	12.7
C_2F_5	119	32.2
C_2F_4	100	7.0
C_2F_3O	97	4.2
CF_3	69	100.0

Preparation of the fluoroxy adduct of $(CF_3)_3COF$ and perfluorovinyl ether

In a typical run, excess (I) (0.5 g) was condensed on to an evacuated frozen solution consisting of 0.3 g of (III) in 2 g of n-C_5F_{12} at a temperature of −196 °C. The solid mixture was then warmed slowly to ambient temperature for a period of 1.5 h, chilled to 0 °C and evacuated at 0 °C leaving an almost quantitative yield of residual clear liquid product (IV). The vapor pressure of the latter was less than 5 mmHg at 25 °C and any isomeric impurities were present in less than 5% concentration.

The IR spectrum of (IV) exhibited no bands in the 2.5 - 7.2 μ region and a strong absorption in the 7.3 - 9.0 μ region (C—F) together with others. The ^{19}F NMR spectrum exhibited nine peaks: δ 72.8 ppm [triplet, a, J(ab)= 9.6 Hz, relative peak area 10, 9F, $C(C\underline{F}_3)_3$], 87.7 ppm [dectet, b, J(ab) = 9.6 Hz, relative peak area 2.4, 2F, $C\underline{F}_2$], 83.8 ppm [multiplet, c, relative peak area 2.8, 2F, $C\underline{F}_2$], 90.3 ppm [complex peaks, d, relative peak area 1.8, 2F, $C\underline{F}_2$], 147 ppm [triplet, f, J = 10 Hz, relative peak area 1.2, 1F, $C\underline{F}$], 82.6 ppm [doublet + multiplet, e, J = 23 Hz, relative peak area 3.2, 3F, $C\underline{F}_3$], 85.3 ppm [multiplet, g, relative peak area 1.8, 2F, $C\underline{F}_2$], 132.1 ppm [singlet, h, relative peak area 4.0 due to a quartet caused by probable impurity from (III), 2F, $C\underline{F}_2$] and 84.2 ppm [multiplet, i, relative peak area 4.4, 3F, $C\underline{F}_3$]. Table 1 shows the mass spectrum (LKB 9000) of (IV). In this table the ions are given in decreasing order of mass numbers, the intensities being relative to the largest peak (CF_3^+ ion, mass m/e value of 69) taken as 100 in the

Fig. 2. Field ionization mass spectrum of product (IV).

relative abundance scale. The peaks of relative abundance below 0.1 for masses greater than 400 and below 2.0 for masses less than 400 have been omitted. The parent ions of these perfluorinated compounds are usually absent from conventional electron-impact mass spectra because of the instability of the molecular ions. The maximum peak was found at a mass *m/e* value of 651 (parent ion minus one oxygen and one fluorine atom). The field ionization mass spectrum exhibited a peak at a mass *m/e* value of 686 as shown in Figure 2, corresponding to the parent ion of the product.

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