Ozonolysis of perfluoroalkenes and perfluorocycloalkenes

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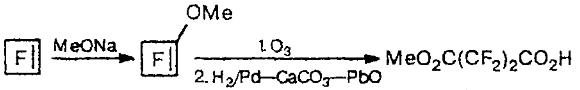
Ozonolysis of 1-methoxyperfluorocyclobutene in Freon-113 followed by hydrogenation of the reaction products gave methyl hydrogen perfluorosuccinate. Under similar conditions, perfluorooct-1- and -2-enes and 4-trifluoromethyl-1,1,1,2,3,4,5,5,5-nonafluoropent-2-ene were converted into perfluorinated heptanoic, hexanoic, and isobutyric acids, respectively.

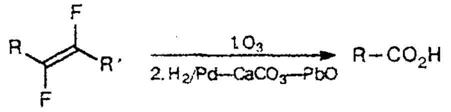
Key words: perfluorocycloalkenes, ozonolysis, reduction, Lindlar catalyst, perfluorocarboxylic acids.

Ozonolysis of perfluoroalkenes has been accomplished only for lower homologs of this series.[1,2] Conjugated oxidation of perfluorooct-1-ene and perfluorooct-2-ene and CF_3CO_2H in the process of their joint ozonation has also been reported.[3–5] The resulting perfluorocarboxylic acid fluorides were identified by ^{19}F NMR and GLC, but were not isolated. Perfluorocyclohexene does not change under these conditions.[5]

We developed a method of ozonolysis of perfluoroalkenes in Freon-113.[6] Under these conditions, perfluorocyclobutene (**1**) yields only traces of an oxygen-containing product. However, 1-methoxyperfluorocyclobutene (**2**) prepared from olefin **1** by nucleophilic substitution of the vinylic fluorine atom does undergo the ozonolysis.[7–9] Treatment of **2** with a fivefold excess of O_3 followed by hydrogenation of the ozonolysis products over the Lindlar catalyst, *i.e.*, under the conditions of "reductive ozonolysis",[1] yields methyl hydrogen tetrafluorosuccinate (**3**) in a yield of 60% instead of the expected ester of perfluorosuccinaldehydic acid. Ozonolysis of perfluoroalkenes **4—6** under the same conditions leads to perfluorocarboxylic acids (**7—9**) in 86, 80, and 74% yields, respectively.



1 **2** **3**



4—6 **7—9**

4: R = $CF_3(CF_2)_5$, R' = F
5: R = $CF_3(CF_2)_4$, R' = CF_3
6: R = $(CF_3)_2CF$, R' = CF_3

7: R = $CF_3(CF_2)_5$
8: R = $CF_3(CF_2)_4$
9: R = $(CF_3)_2CF$

The structures of compounds **3** and **7—9** were confirmed by spectral methods. The IR spectra of perfluorinated acids **3**, **7—9** are characterized by regular displacement of the band of the carbonyl group to shorter wavelengths (ν 1760—1770 cm^{-1}), which is due to the decrease in its electron density caused by highly electronegative fluorine atoms.[10] The ^{13}C NMR spectrum of compound **3** exhibits two triplets (δ 160.17, $^2J_{CF}$ = 24 Hz and δ 161.33, $^2J_{CF}$ = 30 Hz) in the region typical of the resonance of carbonyl carbon atoms; the difluoromethylene groups are manifested as two triplet-triplet signals with close chemical shifts (δ 108.13, $^1J_{CF}$ = 263.8, $^1J_{CF}$ = 30.6 Hz and δ 108.18, $^1J_{CF}$ = 265.3, $^2J_{CF}$ = 31.2 Hz); a singlet corresponding to the methoxy group is observed at δ 54.48. The signals in the ^{13}C NMR spectrum of compound **3** were assigned using a pulse sequence of J-modulated spin echo (JMOD). The ^1H NMR spectrum of compound **3** contains two singlets with a ratio of intensities of 3:1. The narrow singlet at δ 3.94 corresponds to the methoxycarbonyl group, while the broadened singlet is due to the carboxyl group; the position of this signal (δ 7.8—11.35) changes as a function of the concentration of the substance (12.5—50 mg mL^{-1}) and the temperature of the solution (−55 to 50 °C). Increases in the temperature and dilution of the solution are favorable for the cleavage of the intramolecular hydrogen bond, which leads to an upfield shift of the signal of the carboxyl group in the spectrum of compound **3**.[11]

In the mass spectra of both the initial compound **2** and the product of its ozonolysis **3**, the largest mass number corresponds to an ion with *m/z* 174. However, in the case of alkene **2**, this is the molecular ion (its molecular formula is $C_5H_3F_5O$), whereas in the case of compound **3**, the ion with *m/z* 174 ($C_4H_2O_3F_4$) results from abstraction of a HCHO molecule from M^+ and the molecular ion itself is not recorded. Typical routes of fragmentation of M^+ derived from methoxyalkene **2** are abstraction of CH_2O (*m/z* 144) and of F (*m/z* 155); the peak of the ion with *m/z* 109 (C_3F_3O) is the most

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intense. Conversely, in the mass spectrum of **3**, the ion with *m/z* 109 has a relatively low intensity (5.4%), and its composition corresponds to the formula $C_3H_3F_2O_2$, while the ion with *m/z* 59 ($H_3COC{\equiv}O^+$) accounts for the maximum peak.

The ^{13}C NMR spectra of monocarboxylic acids **7** and **8** with an α-CF_2 group contain characteristic triplets at δ 160.12 (J_{CF} = 28.6 Hz) and δ 160.62 (J_{CF} = 38.6 Hz), respectively, due to the carboxyl groups, and the signal for the carboxyl group in acid **9**, which contains an α-CF group, is a doublet at δ 160.2 (J_{CF} = 19.9 Hz). The chemical shifts of the terminal CF_3 groups in linear acids **7** and **8** coincide (δ 117.5), and the signals are quartets of triplets ($^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 33.0 Hz), whereas the signal of the CF_3 groups in acid **9** is a quartet of doublets ($^1J_{CF}$ = 283 Hz, $^2J_{CF}$ = 27.8 Hz) recorded at δ 122. The difluoromethylene groups adjacent to the carboxyl group in compounds **7** and **8** are manifested in the region of δ 110.5 as a triplet of triplets with spin-spin coupling constants at the geminal fluorine atoms of 273.4 Hz and 238.2 Hz, respectively, and spin-spin coupling constants at the two vicinal fluorine atoms of 31.9 Hz and 33.0 Hz, respectively. In compound **9**, the fluoromethine group is adjacent to the carboxyl group, and the signal for its carbon atom is exhibited as a doublet (^1J = 212 Hz, δ 89.5) due to the interaction with one geminal fluorine atom; however, owing to the vicinal interaction with the six fluorine atoms of the two CF_3 groups, each element of the doublet is split into a multiplet.

Experimental

IR spectra were recorded on a Specord 75-IR instrument (in thin film or in CCl_4), ^1H and ^{13}C NMR spectra were obtained on a Bruker AM300 spectrometer using tetramethylsilane as the internal standard, and ^{19}F NMR spectra were recorded on a Tesla BS instrument (100 MHz) with $CFCl_3$ as the internal standard. GLC analysis was performed on a Chrom-5 instrument using SE 30 (5%) on Chromaton N-AW-DMCS and He as the carrier gas. Mass spectra were run on a Finnigan-4021 instrument (a 50-m capillary column with a diameter of 0.25 mm using SE-30 as the stationary phase) at 50—270 °C (6 deg min^{-1}) and at an ionizing voltage of 70 eV.

1-Methoxyperfluorocyclobutene (2) was synthesized by a previously described procedure,[7—9] b.p. 87—88 °C. IR, ν/cm^{-1}: 1750 (C=C). MS, *m/z* (I_{rel} (%)): 174 $[M]^+$ (34.9), 155 $[M-F]^+$ (18.3), 144 $[M-HCHO]^+$ (21.1), 140 $[M-F-CH_3]^+$ (5.5), 131 (4.6), 121 (8.3), 112 (11.9), 109 $[C_3F_3O]^+$ (100), 105 (6.4), 100 $[CF_2{=}CF_2]^+$ (4.6), 95 (5.5), 93 (38.5), 81 (35.8), 75 (15.6), 74 (8.3), 62 (3.7), 55 (1.8), 50 (3.7), 43 (2.7).

Ozonolysis of perfluoroalkenes. At 5—10 °C, a mixture of ozone with oxygen was passed for 2 h at a rate of 70 mL h^{-1} (25 mmol of O_3) (the productivity of the ozonizer was 12.5 mmol h^{-1}) through a solution of perfluoroalkene (5 mmol) in Freon-113 (10 mL). The mixture was purged with argon, then the Lindlar catalyst (10 mg) was added, and the mixture was stirred at −20 °C in an atmosphere of H_2 until peroxides were no longer detected (the iodine-starch test); then the catalyst was filtered off, and the filtrate was concentrated.

Methyl hydrogen perfluorosuccinate (3). IR, ν/cm^{-1}: 1770 s, 2400—3600 br.s. ^1H NMR ($CDCl_3$), δ: 3.94 (s, 3 H, OCH_3); 9.8 (s, COOH). ^{13}C NMR ($CDCl_3$), δ: 54.48 (OCH_3); 160.17 (t, C(1), $^2J_{HF}$ = 24.2 Hz); 108.13 (t, C(2)/C(3), $^1J_{CF}$ = 263.8 Hz, $^2J_{CF}$ = 30.6 Hz); 108.18 (t, C(3)/C(2), $^1J_{CF}$ = 265.3 Hz, $^2J_{CF}$ = 31.2 Hz); 161.33 (t, C(4), J_{CF} = 30.0 Hz). ^{19}F NMR ($CFCl_3$), −δ: 120.3—121.14 (m, 4 F, CF_2). MS, *m/z* (I_{rel} (%)): 174 $[M-HCHO]^+$ (6.7), 159 $[M-COOH]^+$ (6.3), 144 $[C_3F_4O_2]^+$ (4.3), 131 (9.6), 129 $[C_3HF_4O]^+$ (6.2), 124 (6.0), 109 $[C_3H_3F_2O_2]^+$ (5.4), 100 $[CF_2{=}CF_2]^+$ (10.0), 81 (16.6), 74 (4.1), 69 (2.4), 59 $[H_3COC{\equiv}O]^+$ (100), 45 (17.4).

Perfluoroheptanoic acid (7), b.p. 46—47 °C (120 Torr), n_D^{27} 1.3119. IR (CCl_4), ν/cm^{-1}: 1760 s, 2400—3600 br.s. ^1H NMR ($CDCl_3$), δ: 10.38 (s, COOH). ^{13}C NMR ($CDCl_3$), δ: 104.4—114.7 (m, C(3), C(4), C(5), C(6)); 110.5 (tt, C(2), $^1J_{CF}$ = 273.4 Hz, $^2J_{CF}$ = 31.9 Hz); 117.5 (qt, C(7), $^1J_{CF}$ = 288.1 Hz, $^2J_{CF}$ = 33.0 Hz); 160.1 (t, C(1), J_{CF} = 28.6 Hz). ^{19}F NMR ($CFCl_3$, —δ): 81.0 (m, 3 F, CF_3); 118.9 (t, 2 F, $F_2C(2)$, $J_{C(2)F-C(3)F}$ = 12.56 Hz); 121.6 (m, 2 F, $F_2C(3)$); 122.7 (m, 4 F, $F_2C(7)$, $F_2C(5)$); 126.1 (tq, 2 F, $F_2C(6)$, $J_{C(6)F-FC(5)}$ = 14.7 Hz, $J_{C(6)F-FC(7)}$ = 3.5 Hz).

Perfluorohexanoic acid (8), b.p. 134—136 °C. IR (CCl_4), ν/cm^{-1}: 1760 s, 2400—3600 br.s. ^1H NMR ($CDCl_3$), δ: 9.55 (s, COOH). ^{13}C NMR ($CDCl_3$), δ: 110.5 (tt, C(2), $^1J_{CF}$ = 238.2 Hz, $^2J_{CF}$ = 33.0 Hz); 105—114 (m, C(3), C(4), C(5)); 117.5 (qt, C(6), $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 33.0 Hz); 160.6 (t, C(1), J_{CF} = 38.6 Hz).

Perfluoroisobutyric acid (9), b.p. 46—48 °C. IR (CCl_4), ν/cm^{-1}: 1710 s and 1770 var, 3200—3450 br.m. ^1H NMR ($(CD_3)_2CO$), δ: 8.0 (s, COOH). ^{13}C NMR (CD_3OD), δ: 89.5 (dm, C(2), $^1J_{CF}$ = 212 Hz); 122.0 (qd, CF_3, $^1J_{CF}$ = 283 Hz, $^2J_{CF}$ = 27.8 Hz); 162.2 (d, C(1), J_{CF} = 19.9 Hz).

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