Some non-typical structures arising from the ozonolysis of 1-methoxyperfluorocyclobut-1-ene

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Ozonolysis of 1-methoxyperfluorocyclobut-1-ene in Freon-113 leads to polyfluoro-containing cyclic products.

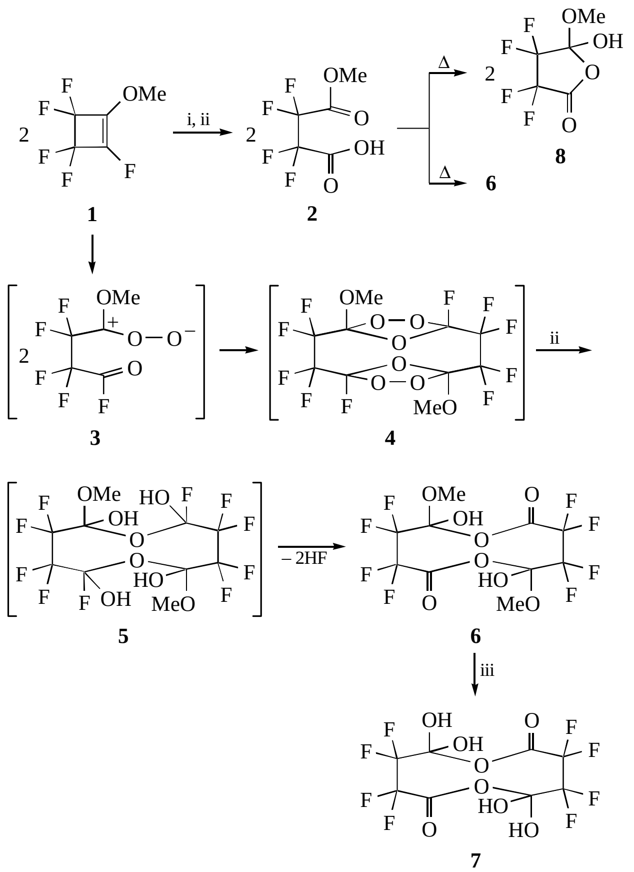
Ozonolysis of the higher ($C \geq 4$) perfluoroalkenes has not been sufficiently studied. The ozonation of perfluoro-1- and oct-2-enes in CF_3COOH is known to give fluoroanhydrides of fluorocarboxylic acids identified by ^{19}F NMR and GLC methods.[1]

Ozonolysis of perfluoroalkenes in Freon-113 leading to perfluorocarboxylic acids has been published by us.[2] In this way, 1-methoxyperfluorocyclobut-1-ene **1** formed 3-methoxycarbonyl-2,2,3,3-tetrafluoropropanoic acid **2**, as confirmed by the ^1H and ^{13}C NMR spectra. A singlet at δ 3.94 ppm (COOMe) and a broad signal at 10 ppm (COOH) were observed in the ^1H NMR spectrum of a solution of **2** in $CDCl_3$, and the ^{13}C NMR spectrum contains a singlet at 54.48 ppm (OMe), two triplet signals at 160.17 ppm ($^2J_{CF}$ 24.2 Hz) and 161.33 ppm ($^2J_{CF}$ 30.0 Hz, CO_2H and CO_2Me) and two triplet–triplet signals at 108.13 ppm ($^1J_{CF}$ 263.8 Hz, $^2J_{CF}$ 30.6 Hz) and 108.18 ppm ($^1J_{CF}$ 265.3 Hz, $^2J_{CF}$ 31.2 Hz, CF_2 groups). An intense band at 1770 cm^{-1} and a wide adsorption band in the 2400–3600 cm^{-1} range appears in IR spectrum of **2** (Nujol).

At the same time, the mass spectrum (MS) of **2**, recorded in negative chemical ionization mode (NCI MS) (HP MS-Engine, HP 5890 Chromatograph, HP-5MS column 30 m × 0.25 mm, temperature 30–200 °C, 6 °C min^{-1}, gas reactant methane, pressure 0.3 Torr, temperature 170 °C) provides evidence for the dimer structure **6** (Scheme 1).

In fact, the NCI MS of the obtained product of ozonolysis of alkene **1**† contains the molecular ion $[M]^-$ (*m*/*z* 408) corresponding to dimer **6** and highly intense ions *m*/*z* 407 and 388 corresponding to the elimination of H atom and HF molecule, respectively, from $[M]^-$. The ions *m*/*z* 204, 203 and 184 characterizing the decomposition of $[M]^-$ of dimer **6** to monomeric products (dedimerization) are also remarkable: $[M/2]^-$, $[M/2 - H]^-$ and $[M/2 - HF]^-$, and the intensity of the latter is a maximum in the spectrum.‡ One possible method of forming dimer **6** in the ion source of the mass spectrometer is thought by us to be less probable, which is to form the latter during ozonolysis of **1** as a result of zwitterion dimerization of **3** (ozonolytic decomposition of alkenes was stated to proceed *via* a bipolar ion of that type[3]) to give cyclic bis(α-methoxy-α-fluoroozonide) **4**. The following reducible (H_2/Pd–$CaCO_3$) decomposition of the peroxidic bridge typical of ozonides[4] leads to intermediate **5**, which loses HF from unstable α-fluorohydrine groups to give bis(α-methoxylactol) **6** (Scheme 1).

That compound **6** is the cyclic dimer of **2** follows from consideration of the intermolecular interaction of carboxylic and methoxycarbonylic groups leading to cyclization. The results obtained confirmed that cyclic dimer **6** was preferable, rather than an alternative monomeric cyclic form **8**, which might be formed due to an intramolecular interaction of COOH and COOMe groups in **2** and was evidently realized in the form of ions during dedimerization of **6** in the ion source of the mass



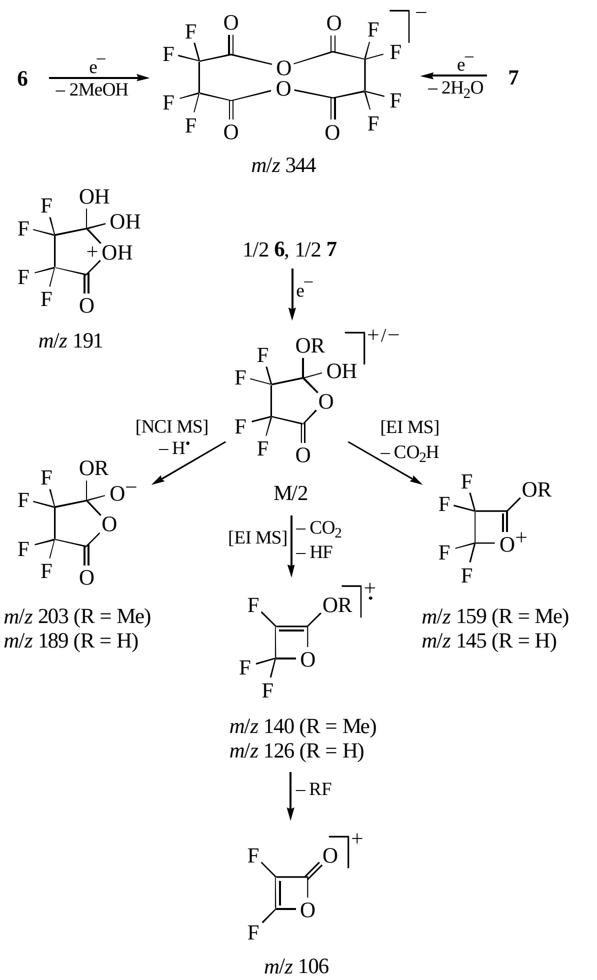
Scheme 1 *Reagents and conditions*: i, O_3/Freon-113, 0–5 °C; ii, H_2/Pd–$CaCO_3$, *ca.* 20 °C; iii, H_2O.

† At 0–5 °C, an O_2/O_3 mixture was passed for 2 h at the rate 30 ml h^{-1} (25 mmol of O_3) (the productivity of the ozonizer was 12.5 mmol h^{-1}) through a solution of **1** (0.78 g, 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). The catalyst was then filtered off and the filtrate evaporated to yield 0.61 g (60%) of **6**.

‡ MS for compounds **6** and **7**.

6: NCI MS (*m*/*z*, I): 408 (9, $[M]^-$), 407 (84, $[M - H]^-$), 394 (1), 389 (5), 388 (38, $[M - HF]^-$), 344 (9, $[M - 2MeOH]^-$), 300 (1), 204 (3, $[M/2]^-$), 203 (48, $[M/2 - H]^-$), 189 (8), 185 (6), 184 (100, $[M/2 - HF]^-$), 172 (1), 144 (2). EI MS (*m*/*z*, I): 187 (1, $[M/2 - OH]^+$), 173 (0.5, $[M/2 - OCH_3]^+$, 159 (2, $[M/2 - CO_2H]^+$), 145 (3, $[M/2 - CO_2CH_3]^+$), 140 (44, $[M/2 - CO_2 - HF]^+$), 131 (5), 117 (8), 109 (21), 106 (24, $[C_3F_2O_2]^+$), 100 (20, $[CF_2{=}CF_2]^+$), 97 (21), 81 (13), 69 (8), 59 (100, $MeOC{\equiv}O^+$).

7: NCI MS (*m*/*z*, I): 379 (0.5, $[M - H]^-$), 363 (0.5, $[M - OH]^-$), 345 (1), 344 (15, $[M - 2H_2O]^-$), 326 (1, $[M - H_2O - HOF]^-$), 316 (0.5, $[M - 2H_2O - CO]^-$), 300 (1, $[M - 2H_2O - CO_2]^-$), 262 (1, $[M - 2H_2O - CO_2 - F_2]^-$), 244 (0.5), 198 (0.5), 190 (0.5, $[M/2]^-$), 189 (10, $[M/2 - H]^-$), 170 (33, $[M/2 - HF]^-$), 154 (1), 144 (10), 126 (100, $[C_3HF_3O_2]^-$), 106 (21). PCI MS (*m*/*z*, I): 321 (1), 273 (0.5), 247 (1), 231 (2), 229 (1), 219 (1), 218 (1), 205 (5), 191 (100, $[M/2 - H]^+$), 173 (30, $[M/2 - OH]^+$), 145 (9, $[M/2 - CO_2H]^+$), 129 (4), 109 (5), 106 (1). EI MS (*m*/*z*, I): 145 (4, $[M - CO_2H]^+$), 126 (50, $[M - CO_2 - HF]^+$), 117 (6), 109 (27), 106 (76, $[C_3F_2O_2]^+$), 100 (32, $[CF_2{=}CF_2]^+$), 97 (20), 96 (18), 82 (13), 81 (9), 78 (20), 69 (9), 67 (7), 60 (5), 51 (27), 45 (100, $[HOC{\equiv}O]^+$).



Scheme 2

spectrometer. On the other hand, ^{1}H and ^{13}C NMR spectra showed that dimer **6** was transformed to monomer **2** in $CDCl_3$ solution.

Compound **6** was a viscous liquid that was gradually (over a month) transformed to a solid product (mp 83–84 °C). According to spectral data the structure of the latter was bis(α-hydroxylactol) **7**. In contrast to **6**, the IR spectrum of **7** (in Nujol) showed the carbonyl band to be shifted to the low frequency area (ν = 1700 cm^{-1}), and in the OH area vibrations an intense band due to hydroxylic groups (ν = 3390 cm^{-1}, $W_{1/2}$ = 280 cm^{-1}) was observed. In the ^{1}H NMR spectrum of a solution of **7** in $CDCl_3$ a hydroxyl signal was observed at 5.1 ppm ($W_{1/2}$ = 30 Hz), while a signal at *ca.* 4 ppm (OMe) was absent. Unfortunately, the ^{13}C NMR spectrum of **7** was not recorded due to its low solubility. The NCI MS for compound **7** was observed to be very significant, as in the case of **6**. The distinctive ion *m*/*z* 344, evidently formed as a result of elimination of two molecules of water from [M]$^-$ (Scheme 2), was assigned from the spectrum of **7** together with the ion [M – H]$^-$ (*m*/*z* 379). The ion *m*/*z* 344, but at half the relative intensity was observed in the NCI MS of **6**; its formation was caused by the removal of two methanol molecules from [M]$^-$. The formation of other ions in the NCI MS of **7** was also readily interpretated. Thus, analogously to the dedimerization process of dimer **6** observed in NCI MS, the spectra of the compound **7** showed ions *m*/*z* 189 ([M/2 – H]$^-$) and 170 ([M/2 – HF]$^-$) reflecting the decomposition to monomer fragments. The structure **7** was confirmed by MS recorded in a positive chemical ionization (PCI MS) mode. Ion *m*/*z* 395, reflecting the protonated molecular ion [M + H]$^+$, was present in the spectrum, and ion *m*/*z* 191, corresponding to ion [M/2 + H]$^+$, (Scheme 2) was the most abundant. The stability of the *m*/*z* 191 ion was in agreement with the known high resistance of hydrates and semiacetales of α,α-difluorosubstituted carbonyl compounds.[5]

Fragmentation methods following dedimerizations were shown to be similar for electron impact (EI MS) of compounds **6** and **7**. Thus, ions *m*/*z* 145 and 126 in EI MS of **7**, which are highly intense and differ by 14 mass units, respectively, correspond to ions *m*/*z* 159 and 140, which are characteristic of EI MS of **6** and possess the same high intensity. Note that both routes of fragmentation result in the same ion *m*/*z* 106 (Scheme 2). Ion *m*/*z* 59 was found to be the maximum one in the EI MS of **6**, whereas in the EI MS of **7** ion *m*/*z* 45 was recorded to be the maximum, which confirmed the ester nature of compound **6**, whereas the compound **7** was found to be a hydrolysis product of **6**.

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