Ozonides of perfluorooct-1-ene and perfluorooct-2-ene

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Ozonides of higher perfluoroalkenes were prepared for the first time by ozonation of perfluorooct-1- and -2-enes in Freon-113. The structures of the resulting compounds were confirmed by ^{13}C NMR spectroscopy and GLC-mass spectrometry.

Key words: perfluoroalkenes, ozonolysis, ozonides, GLC-mass spectrometry, ^{13}C NMR spectroscopy.

Ozonides of alkenes containing perfluoroalkyl substituents at the double bond[1] and of perfluoroethylene[2] are known. Ozonolysis of higher ($C \geq 4$) perfluoroalkenes remains poorly studied.[3] Ozonolysis of cyclic and acyclic perfluoroalkenes in Freon-113 afforded the corresponding perfluorocarboxylic acids.[4]

In the present work, we studied the reactions of ozone with perfluorooct-1- and -2-enes (**1** and **2**, respectively). Ozonation of these compounds as solutions in Freon-113 (CCl_2FCClF_2) yielded ozonides **3** and **4**, respectively (Scheme 1), which was confirmed by spectral data.

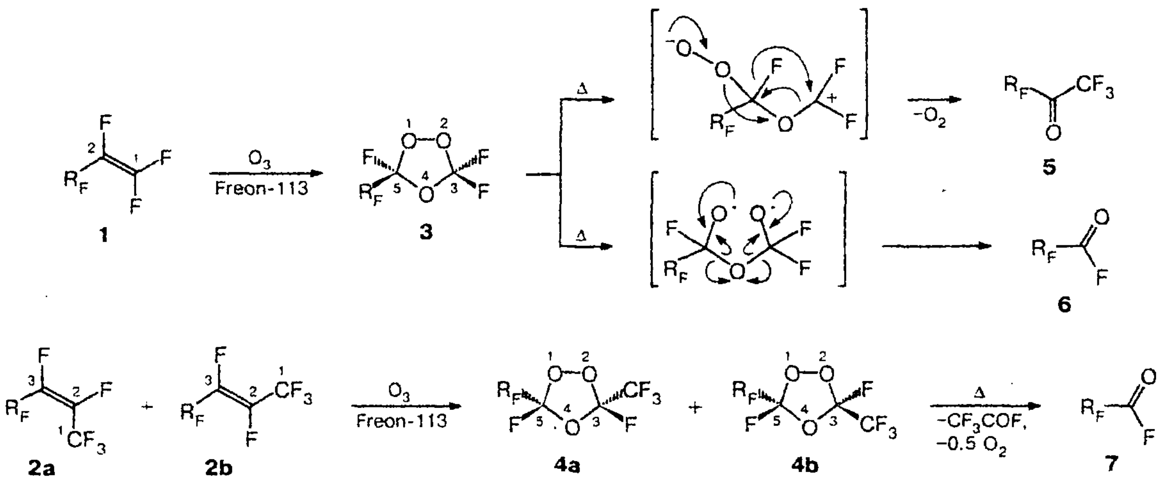
The structure of ozonide **3** was established based on its ^{13}C NMR spectrum. This spectrum has a signal as a doublet of triplets characteristic[5] of the CF group in the trioxolane ring (at $\delta \geq 120$) and a signal for the 3-CF_2 group as a doublet of doublets in the region free of other signals (at δ 129.5), which is indicative of the nonequivalence of the geminal F atoms.

Ketone **5** ($\tau_{rel} = 1.04$) and acyl fluoride **6** ($\tau_{rel} = 1.00$) were detected along with ozonide **3** (a peak with $\tau_{rel} = 1.07$) in a ratio of 1 : 4 : 2.5 by GLC-mass spectrometry. The highest ion peak in the chemical-ionization positive ion mass spectrum (CIPIMS) of ozonide **3** is observed at m/z 417. This peak is associated with elimination of the O_2 molecule from the $[M + H]^+$ ion. This fragmentation has been noted previously in studies of nonfluorinated ozonides.[6] The $[M + H]^+$ ions also lose OH, HOF, and CF_2 groups to give peaks of ions at m/z 400, 381, and 367, respectively.

In the chemical-ionization negative ion mass spectrum (CINIMS) of ozonide **3**, the peak of the $[M]^-$ ion is absent. This spectrum has peaks of the fragmentation ions $[M - F - CO_2]^-$ (m/z 385), $[M - F_2 - CO_2]^-$ (m/z 366), and $[M - F - COF_2]^-$ (m/z 344).

The CIPIMS of ketone **5** and acyl fluoride **6** have peaks of the corresponding protonated $[M + H]^+$ molecular ions (at m/z 417 and 367, respectively), and their

Scheme 1



$R_F = CF_3(CF_2)_5$ (**1**, **3**, **5**, **6**); $CF_3(CF_2)_4$ (**2a,b**, **4a,b**, **7**)

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CINIMS have $[M]^-$ molecular ion peaks (at *m/z* 416 and 366, respectively). Since the ^{13}C NMR spectrum of ozonide **3** has no signals belonging to ketone **5** (the $COCF_3$ group)[7] and acyl fluoride **6** (the COF group),[7] it can be concluded that compounds **5** and **6** are formed as a result of thermal decomposition of ozonide **3**. Actually, both the homolytic cleavage of the peroxide bridge[8] and the heterolytic cleavage of the C—O bond to form a zwitterion[9] are typical of thermal decomposition of ozonides. Thus, the formation of ketone **5** and acyl fluoride **6** in the course of GLC-mass spectrometric analysis can be readily rationalized (see Scheme 1).

Ozonation of perfluoroalkene **2** consisting of the *Z*- (**2a**) and *E*-isomers (**2b**) (1.0 : 2.4) afforded a mixture (~1:1) of *cis*- (**4a**) and *trans*-ozonides (**4b**) (the data from GLC-mass spectrometry). This result is consistent with the published data[10] according to which mixtures containing *cis*- and *trans*-ozonides in virtually equal ratios are formed regardless of the stereochemistry of the initial alkene. This fact supports the zwitterionic mechanism of the ozonolysis of alkenes.[11]

The chemical-ionization positive ion mass spectra of *cis*- (**4a**) and *trans*-ozonides (**4b**) are substantially different. Only the mass spectrum of the (supposedly) *cis*-isomer **4a** has the $[M + H]^+$ ion peak (*m/z* 449). This ion is stabilized due apparently to the sterically more favorable formation of hydrogen bonds[12] compared to *trans*-isomer **4b** (Scheme 2).

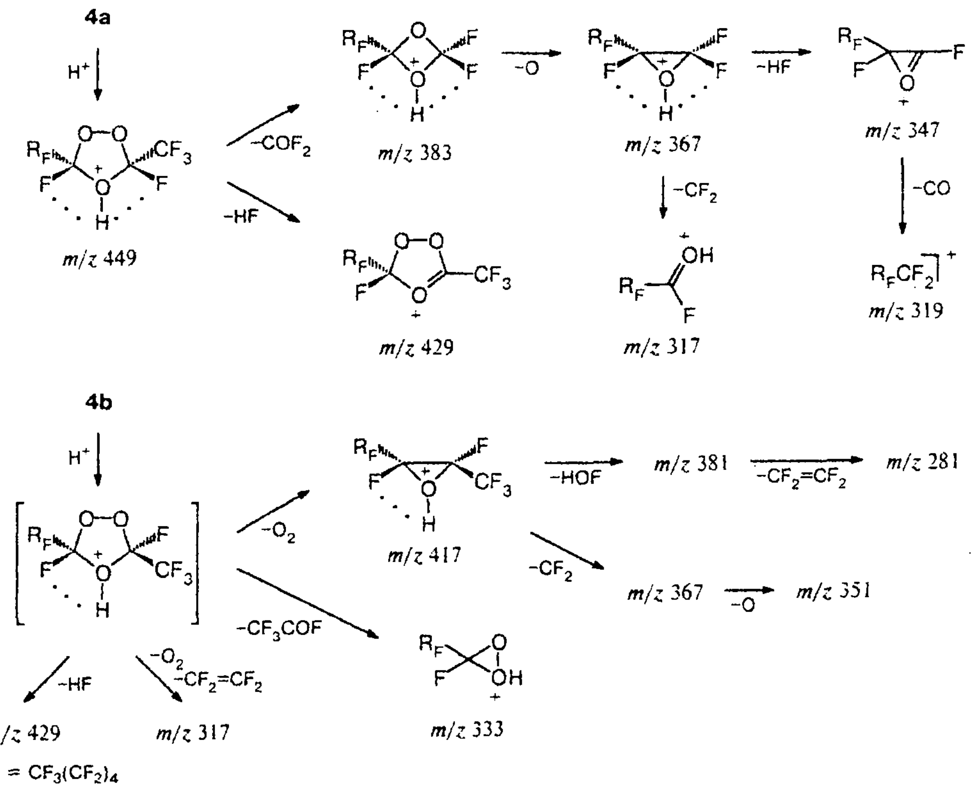
Apparently, for the same reason the fragmentation of the $[M + H]^+$ ion in *cis*-ozonide **4a** with elimination of the COF_2 molecule occurred with retention of hydrogen bonds in the resulting $[C_7HF_{14}O_2]^+$ ion (*m/z* 383). On the contrary, the $[M + H]^+$ ion peak is absent in the mass spectrum of *trans*-ozonide **4b**, and the major fragmentation paths involve elimination of the O_2 and $CF_2{=}CF_2$ molecules. The presence of the intense $[M + H - HF]^+$ ion peak (*m/z* 429) is the common feature of the mass spectra of both stereoisomers **4a** and **4b** (see Scheme 2).

Thermal decomposition of ozonides **4a** and **4b** under conditions of GLC-mass spectrometry afforded acyl fluoride **7** (see Scheme 1) (τ_{rel} = 1.22, 1.14, and 1.00, respectively; the ratio **4a** : **4b** : **7** = 1 : 1 : 2). The CIPIMS and CINIMS of acyl fluoride **7** have the $[M + H]^+$ and $[M]^-$ ion peaks, respectively.

Experimental

The IR spectra were recorded on a Specord 75-IR instrument (in Nujol mulls). The ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer. The GLC-mass spectrometric studies were carried out on an HP MS-Engine instrument equipped with an HP 5890 chromatograph; the splitting coefficient was 1 : 50; an HP-5MS column (30 m × 0.25 mm), the flow rate was 35 $cm^3 s^{-1}$; thermostatic control at 32 °C for 5 min; then the temperature was raised to 200 °C (6 deg min^{-1}); methane was used as the reagent gas; the pressure in the ion source was 0.3 Torr and

Scheme 2



the temperature was 170 °C; the EI parameters were as follows: the ionizing voltage was 70 eV and the temperature was 200 °C.

Pefluorooct-1-ene (1) and perfluorooct-2-ene (2) were prepared according to a known procedure.[13] **For alkene 1.** IR, ν/cm^{-1}: 1645 w, 1775 (s, C=C). ^{13}C NMR ($CDCl_3$—CCl_2FCClF_2), δ: 107.2—123.6 (m, C(4), C(5), C(6), C(7)); 118.1 (qt, C(8), $^1J_{CF}$ = 287.8 Hz, $^2J_{CF}$ = 32.9 Hz); 121.2 (dtt, C(2), $^1J_{CF}$ = 300.3 Hz, $^2J_{CFC(1)}$ = 39.3 Hz, $^2J_{CFC(3)}$ = 34.8 Hz); 156.48 (td, C(1), $^1J_{CF}$ = 295.8 Hz, $^2J_{CF}$ = 39.5 Hz). MS (EI), *m/z* (I_{rel} (%)): 400 $[M]^+$ (5.4), 381 $[C_8F_{15}]^+$ (5.8), 331 (1.0), 281 $[C_6F_{11}]^+$ (0.9), 231 $[C_5F_9]^+$ (1.4), 181 $[C_4F_7]^+$ (6.3), 169 (3.9), 162 (4.0), 131 $[C_3F_5]^+$ (100), 119 (10.2), 100 $[C_2F_4]^+$ (6.1), 93 (11.2), 69 $[CF_3]^+$ (39.3); (CIPI): 400 $[M]^+$ (3.0), 381 $[M - F]^+$ (100), 363 (0.2), 362 (0.3), 331 (0.2), 281 (0.1), 231 (0.3), 209 (0.3), 195 (0.5), 181 (0.9), 169 (0.2), 162 (0.4); CINI: 400 $[M]^-$ (100), 381 $[M - F]^-$ (1.8), 362 $[M - F_2]^-$ (6.0), 331 (0.8), 281 $[M - C_2F_5]^-$ (16.1), 262 (1.4), 231 (2.6), 212 (0.5).

For alkene 2 (*Z*/*E* = 1.0:2.4), IR, ν/cm^{-1}: 1705 m, 1775 (s, C=C). ^{13}C NMR ($CDCl_3$—CCl_2FCClF_2), δ: 104.0—115.3 (m, C(4), C(5), C(6), C(7)); 118.0 (qt, C(8), $^1J_{CF}$ = 286.9 Hz, $^2J_{CF}$ = 33.0 Hz); 111.9—124.8 (m, C(1)); 140.1—144.8 (m, C(2)); 142.1—147.1 (m, C(3)). CIPIMS, *m/z* (I_{rel} (%)): 400 $[M]^+$ (0.6), 381 $[M - F]^+$ (100), 363 (0.6), 362 (0.4), 359 (0.3), 341 (0.3), 331 (0.1), 281 (0.2), 231 (0.2), 209 (0.2), 181 (1.8), 169 (0.1), 162 (0.2), 159 (0.2), 131 (1.8), 100 (0.1), 93 (0.2), 69 (0.5); CINIMS: 400 $[M]^-$ (100), 381 $[M - F]^-$ (0.5), 362 $[M - F_2]^-$ (1.1), 331 (0.1), 281 (2.6), 262 (0.1), 231 (0.5)

For *Z*-alkene 2a (τ_{rel} = 1.03). MS (EI), *m/z* (I_{rel} (%)): 400 $[M]^+$ (3.8), 381 $[M - F]^+$ (16.5), 331 (2.0), 293 (2.3), 281 $[C_6F_{11}]^+$ (6.5), 243 (2.4), 231 $[C_5F_9]^+$ (5.1), 181 $[C_4F_7]^+$ (100), 169 (9.3), 162 (5.8), 131 $[C_3F_5]^+$ (76.7), 119 (16.3), 100 $[C_2F_4]^+$ (5.2), 93 (13.3), 69 $[CF_3]^+$ (45.4).

For *E*-alkene 2b (τ_{rel} = 1.0, τ = 1.73 min). MS (EI), *m/z* (I_{rel} (%)): 400 $[M]^+$ (5.9), 381 $[M - F]^+$ (29.3), 331 (2.1), 293 (2.1), 281 $[C_6F_{11}]^+$ (10.4), 243 (2.8), 231 $[C_5F_9]^+$ (5.7), 181 $[C_4F_7]^+$ (100), 169 (8.6), 162 (7.0), 131 $[C_3F_5]^+$ (74.5), 119 (17.0), 100 $[C_2F_4]^+$ (6.5), 93 (14.9), 69 $[CF_3]^+$ (51.4).

Ozonolysis of perfluorooct-1-ene (1) and perfluorooct-2-ene (2). An ozone—oxygen mixture was passed through a solution of alkene **1** or **2** (a mixture of (*Z*)-**2a** and (*E*)-**2b**, 1.0:2.4) (2.0 g, 5.0 mmol) in Freon-113 (10 mL) at a rate of 30 L h^{-1} at 15—20 °C for 2 h (25 mmol of O_3) (the performance of the ozonizer was 12.5 mmol h^{-1}). The mixture was purged with argon and the solvent was evaporated at room temperature. The residue contained ozonide **3** or **4** (a mixture of the *cis*- (**4a**) and *trans*-isomers (**4b**), 1 : 1), respectively.

3,3,5-Trifluoro-5-perfluorohexyl-1,2,4-trioxolane (3). ^{13}C NMR ($CDCl_3$—CCl_2FCClF_2), δ: 104.9—116.0 (m, C(1′), C(2′), C(3′), C(4′), C(5′)); 118.1 (qt, C(6′), $^1J_{CF}$ = 287.6 Hz, $^2J_{CF}$ = 32.8 Hz); 120.5 (dt, C(5), $^1J_{CF}$ = 292.9 Hz, $^2J_{CF}$ = 30.5 Hz); 129.5 (dd, C(3), $^1J_{CF}$ = 277.5 and 262.1 Hz).

A mixture (1:1) of *cis* (4a) and *trans*-3,5-difluoro-5-perfluoropentyl-3-trifluoromethyl-1,2,4-trioxolanes (4b). ^{13}C NMR ($CDCl_3$—CCl_2FCClF_2), δ: 104.2—123.4 (m, C(3), C(5), C(1′), C(2′), C(3′), C(4′)); 110.4—123.3 (m, $\underline{C}F_3$—C(3)); 118.0 (qt, C(5′), $^1J_{CF}$ = 287.6 Hz, $^2J_{CF}$ = 34.7 Hz).

GLC-mass spectrometric analysis of ozonides 3 and 4. Ozonide 3 (τ_{rel} = 1.07). CIPIMS, *m/z* (I_{rel} (%)): 417 $[(M + H) - O_2]^+$ (1.3), 400 (1.3), 381 $[C_8F_{15}]^+$ (100), 367 $[(M + H) - O_2 - CF_2]^+$ (9.2), 363 (1.0), 343 (0.7), 319 (1.2), 243 (0.8); CINIMS: 400 $[M - O_3]^-$ (0.5), 385 $[M - F - CO_2]^-$ (4.5), 366 $[M - F_2 - CO_2]^-$ (100), 363 $[M - F - COF_2]^-$ (3.2), 344 $[M - F_2 - COF_2]^-$ (32.3), 328 $[M - 2F_2 - CO_2]^-$ (4.8), 300 $[C_6F_{12}]^-$ (5.2), 294 (1.6), 262 $[C_6F_{10}]^-$ (1.0), 244 $[M - F_2 - COF_2 - C_2F_4]^-$ (5.1).

Ketone 5 (τ_{rel} = 1.04). CIPIMS, *m/z* (I_{rel} (%)): 457 $[M + C_3H_5]^+$ (0.5), 445 $[M + Et]^+$ (2.3), 417 $[M + H]^+$ (100), 397 $[M - F]^+$ (16.7), 395 (12.8), 381 $[M - OF]^+$ (24.9), 281 (11.1), 231 (4.2), 219 (2.4), 181 (1.9), 169 (2.9); CINIMS: 435 $[M + F]^-$ (2.0), 416 $[M]^-$ (15.8), 381 (0.8), 378 $[M - F_2]^-$ (2.9), 362 (2.8), 350 $[M - COF_2]^-$ (11.3), 331 (4.5), 281 (12.5), 231 (7.0).

Acyl fluoride 6 (τ_{rel} = 1.00, τ = 1.71 min). CIPIMS, *m/z* (I_{rel} (%)): 367 $[M + H]^+$ (100), 347 $[M - F]^+$ (2.4), 319 $[M - COF]^+$ (9.5); CINIMS: 385 $[M + F]^-$ (2.7), 366 $[M]^-$ (100), 328 $[M - F_2]^-$ (3.8), 300 $[M - COF_2]^-$ (2.1).

***cis*-Ozonide 4a** (τ_{rel} = 1.22). CIPIMS, *m/z* (I_{rel} (%)): 449 $[M + H]^+$ (1.7), 429 $[M - F]^+$ (100), 383 $[(M + H) - COF_2]^+$ (86.0), 367 $[(M + H) - COF_2 - O]^+$ (73.0), 347 $[(M + H) - COF_2 - O - HF]^+$ (3.3), 319 $[(M + H) - COF_2 - O - HF - CO]^+$ (22.8), 317 $[(M + H) - COF_2 - O - CF_2]^+$ (11.4), 301 (11.2), 267 (5.7), 231 (9.0), 217 (5.0).

***trans*-Ozonide 4b** (τ_{rel} = 1.14). CIPIMS, *m/z* (I_{rel} (%)): 429 $[M - F]^+$ (68.1), 417 $[(M + H) - O_2]^+$ (2.2), 381 $[C_8F_{15}]^+$ (78.6), 367 $[(M + H) - O_2 - CF_2]^+$ (33.3), 351 $[(M + H) - O_2 - CF_2 - O]^+$ (16.9), 333 $[(M + H) - CF_3COF]^+$ (57.2), 317 $[(M + H) - O_2 - C_2F_4]^+$ (100), 316 (50.2), 281 $[C_6F_{11}]^+$ (19.1), 269 (35.0), 251 (11.3), 217 (9.5).

Acyl fluoride 7 (τ_{rel} = 1.00, τ = 1.63 min). CIPIMS, *m/z* (I_{rel} (%)): 317 $[M + H]^+$ (100), 297 $[M - F]^+$ (2.4), 269 $[M - COF]^+$ (15.4); CINIMS: 335 $[M + F]^-$ (13.7), 316 $[M]^-$ (100), 278 $[M - F_2]^-$ (1.8), 250 $[M - COF_2]^-$ (2.2).

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