

Ozonolysis of Alkenes and Studies of Reactions of Polyfunctional Compounds: LXV.* Ozonolysis of Perfluoro-1-octene in Freon-113

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Abstract—Ozonization of perfluoro-1-octene in Freon-113 yields the corresponding ozonide whose catalytic hydrogenation over Pd/C or hydride reduction leads to formation of perfluoroheptanoic acid; the reduction with lithium aluminum hydride gives 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-heptanol. Ozonization of perfluoro-1-octene in Freon-113 containing excess (≥ 3 equiv) alcohol affords the corresponding perfluoroheptanoic acid ester.

Ozonization of higher (starting from C_4) perfluoroalkenes is difficult to occur, and this reaction has been studied insufficiently [2]. We have developed an efficient procedure for ozonization of such weakly reactive olefins with respect to electrophiles [3].

Study of the ozonolysis of perfluoro-1-octene (**I**) in Freon-113 showed that the primary oxidation product and precursor of perfluoroheptanoic acid (**III**) [3] is the corresponding ozonide, 3,3,5-trifluoro-5-tridecafluorohexyl-1,2,4-trioxolane (**II**), which was isolated as a ~1:1 mixture with Freon-113 by concentrating the reaction mixture. The ^{13}C NMR spectrum** of the product contained two doublets typical of C^3 in trioxolane ring. These doublets were characterized by different ^{13}C - ^{19}F coupling constants due to interaction with nonequivalent fluorine atoms: $^1J(CF') = 277.5$ and $^1J(CF'') = 262.1$ Hz. The terminal fluorine atoms in the vinyl group of initial olefin **I** are equivalent, and the signal of the $=CF_2$ group appears in the ^{13}C NMR spectrum as a triplet [$^1J(CF) = 295.8$ Hz], each

component of which is split into a doublet [$^2J(CF) = 39.5$ Hz] due to coupling with fluorine nuclei of the neighboring CF group. The signal from the endocyclic CF_2 group in **III** does not suffer the strong negative inductive effect of the C_6F_{13} group, and it is located considerably upfield (δ_C 129.5 ppm) relative to the vinyl CF_2 signal of initial alkene (**I**) (δ_C 156.5 ppm). The CF carbon atom in ozonide **II**, as well as in **I**, is attached to the polyfluoroalkyl group, and its signal appears in the same region as that of alkene **I** (δ_C 120.5 and 121.2 ppm, respectively). It should be noted that the CF signal in the spectrum of **II** is a doublet of triplets (there is no coupling with the endocyclic CF_2 group); the corresponding signal of alkene **I** is a double triplet of triplets.

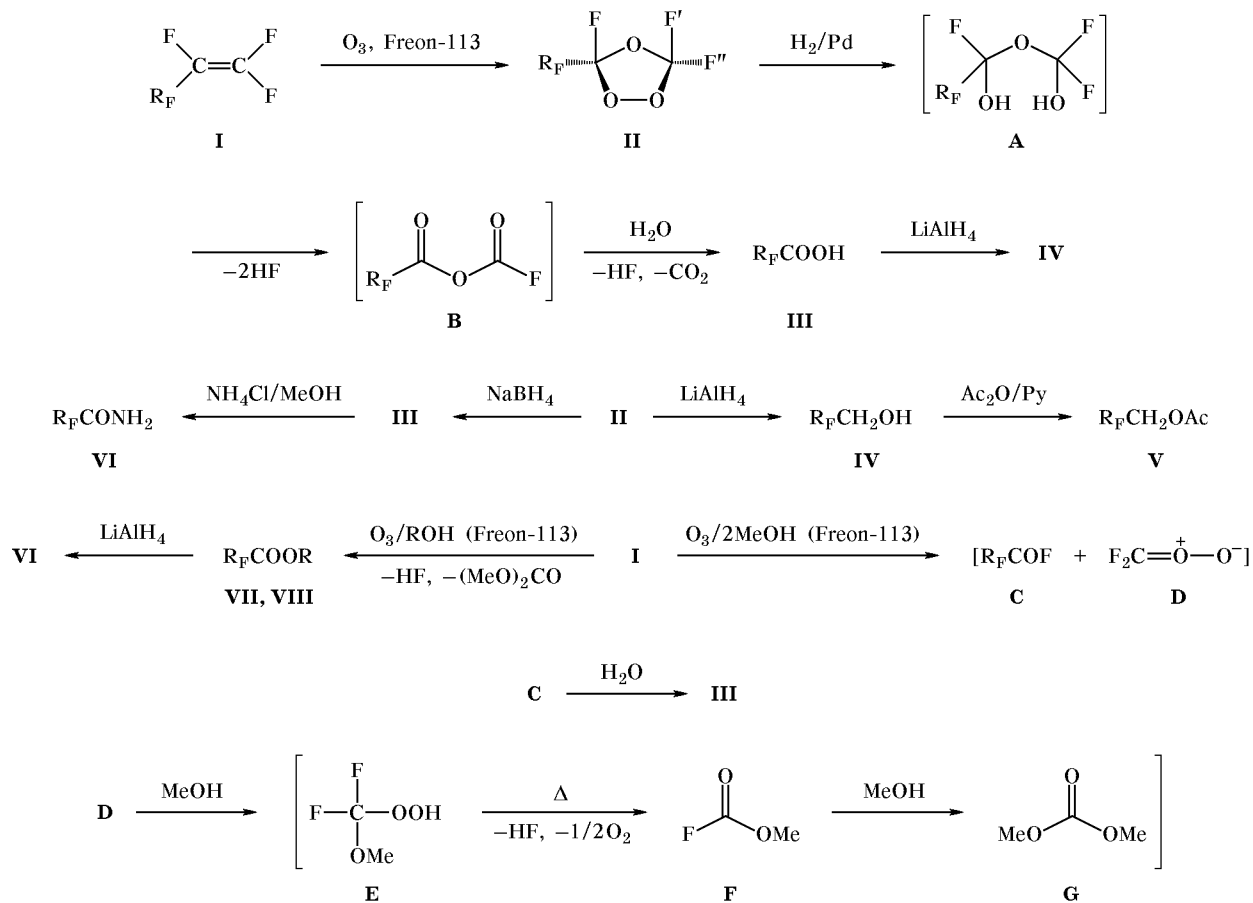
Reduction of ozonide **II** with hydrogen over palladium catalyst yields acid **III**. Presumably, reductive cleavage of the peroxide bridge (which is typical of ozonides) [5, 6] leads to intermediate **A** which loses hydrogen fluoride molecule to form anhydride **B**, and the latter is readily hydrolyzed to acid **III** (Scheme 1).

The reduction of ozonide **II** with sodium tetrahydridoborate stops at the stage of formation of acid **III**, whereas lithium aluminum hydride vigorously reacts with **II** yielding tridecafluoroheptanol **IV**. The latter can be converted into the corresponding acetate **V**. Alcohol **IV** was also obtained by reduction

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** The ^{13}C NMR spectrum of **II** was recorded in $CDCl_3$. In the spectrum recorded in acetone- d_6 we observed only signals belonging to acid **III**, presumably due to solvolysis with polar solvent and hydrolysis which are typical processes for nonfluorinated ozonides [4].

Scheme 1.



VII, R = Me; **VIII**, R = Et; R_F = CF₃(CF₂)₅.

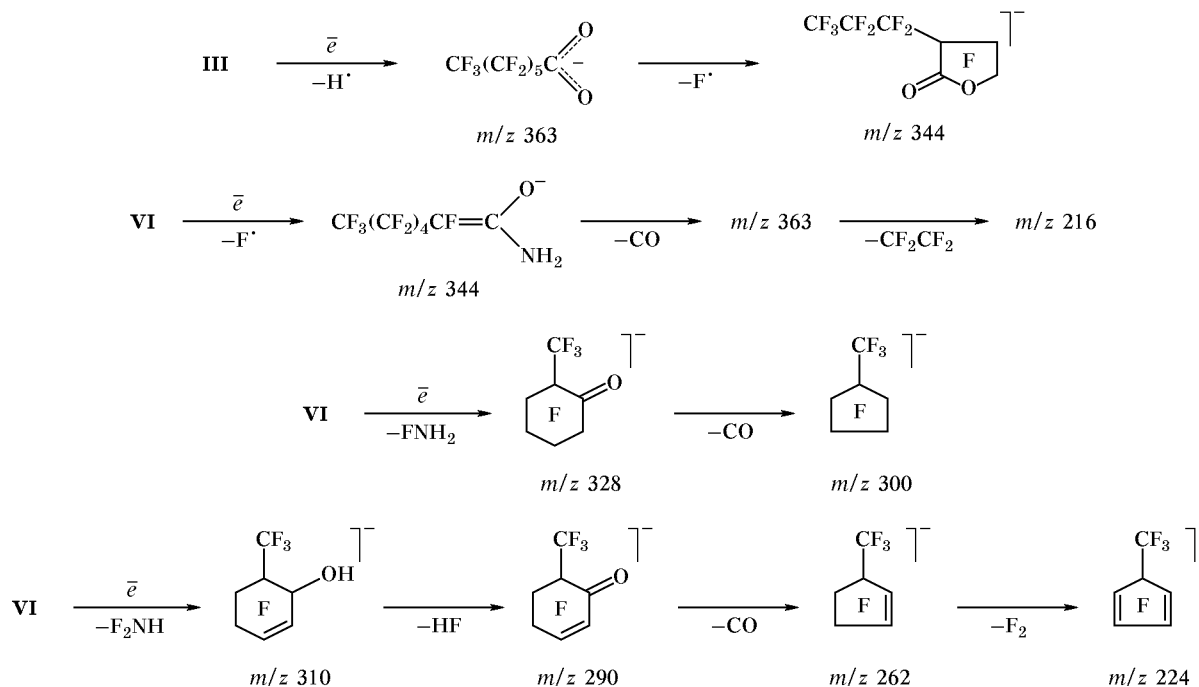
of acid **III** with lithium aluminum hydride. Treatment of acid **III** with ammonium chloride in methanol gave amide **VI** which showed a characteristic mass spectrum. In the positive ion chemical ionization (PICI) mass spectrum the base peak was that of the $[M+H_2]^+$ ion (m/z 365). Only one fragment ion peak was observed in the region of large m/z values (m/z 347); it is formed by elimination of NH_2 from the molecular ion $[M]^+$. The PICI spectrum of **VI** also contained ion peaks with m/z 379 ($[M+\text{CH}_4]^+$) and 393 ($[M+\text{C}_2\text{H}_6]^+$). Amide **VI** showed in the NICI mass spectrum an ion peak with m/z 344 (I_{rel} 100%) which results from abstraction of fluorine atom from the molecular ion $[M]^-$ (Scheme 2). In the NICI mass spectrum of acid **III** the base peak also has m/z value 344, but the corresponding ion is formed by elimination of HF from $[M]^-$; presumably, it has the structure of five-membered lactone (Scheme 2). The NICI mass spectrum of **VI** contains strong peaks with large m/z values which suggest three fragmentation pathways of

the molecular ion. The first of these involves nitrogen-containing ions (m/z 344, 316, 216), and the two other begin with elimination of the FNH_2 (m/z 328, 300) or F_2NH group (m/z 310, 290, 262, 224). Probably, ions with m/z 328, 310, 300, 290, 262, and 224 have a cyclic structure (Scheme 2).

In the electron impact mass spectrum of **VI** we observed an ion peak with m/z 319, arising from cleavage of the C^1-C^2 bond and elimination of the CONH_2 group. The subsequent fragmentation includes successive loss of fluorine atom (m/z 300, 281) and CF_2 group (m/z 231, 181, 131). The most abundant ion is that with m/z 131.

Ozonolysis of alkene **I** in Freon-113 in the presence of at least 3 equiv of alcohol (methanol or ethanol) yields the corresponding perfluoroheptanoic acid esters **VII** and **VIII**. Reduction of the latter with LiAlH_4 affords alcohol **IV** (Scheme 1). On the other hand, ozonization of **I** in the presence of 2 equiv of methanol leads to formation of acid **III**; presumably,

Scheme 2.



the alcohol is consumed for binding of carbonyl difluoride **D** to difluoro(methoxy)methyl hydroperoxide **E** [6] which is then transformed into volatile esters **F** and **G** (Scheme 1).

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films or KBr pellets. The 1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument using $CDCl_3$, CD_3OD , or $CDCl_3$ -Freon-113 ($CF_2ClCFCl_2$) as solvent. Chromatographic analysis (GLC) was performed on a Chrom-5 instrument (stationary phase 5% of SE-30 on N-AW-DMCS, carrier gas helium). Silufol plates were used for thin-layer chromatography (development with iodine vapor). The mass spectra were obtained on an HPMS-Engine including an HP-5890 gas chromatograph [split ratio 1:50, 30000 \times 0.25-mm HP-5MS column, flow rate 35 cm/s, oven temperature programming from 32°C (5 min) to 200°C at 6 deg/min, reactant gas methane, ion source pressure 0.3 mm, ion source temperature 170°C; electron impact: 70 eV, temperature 200°C].

3,3,5-Trifluoro-5-tridecafluorohexyl-1,2,4-trioxolane (II). An ozone-oxygen mixture was passed over a period of 2 h (25 mmol of O_3 ; ozonizer efficiency 12.5 mmol of O_3 per hour; flow rate 30 l/h) through a solution of 2 g (5 mmol) of perfluoro-1-

octene (**I**)* in 20 ml of Freon-113, maintained at 0–5°C. The mixture was purged with argon, and the solvent was distilled off almost completely under reduced pressure (water-jet pump). The residue was 2.8 g of a ~1:1 mixture (according to HPLC data) of ozonide **II** and Freon-113. ^{13}C NMR spectrum of **II**, δ_C , ppm (J , Hz): 104.9–116.0 m (CF_2), 118.12 q.t [CF_3 , $^1J(CF) = 287.6$, $^2J(CF) = 32.8$], 120.47 d.t [C^5 , $^1J(CF) = 292.9$, $^2J(CF) = 30.5$], 129.50 d [C^3 , $^1J(CF) = 277.5$], 129.50 d [C^3 , $^1J(CF) = 262.1$]. Found, %: C 23.72. $C_8F_{16}O_3$. Calculated, %: C 24.02.

Perfluoroheptanoic acid (III). a. Alkene **I**, 2 g (5 mmol), in 20 ml of Freon-113 was ozonized as described above. The mixture was purged with argon, 0.01 g of 5% Pd/C was added, and the mixture was stirred under hydrogen (~12 h) until it showed a negative test for peroxides (starch-iodine). The catalyst was filtered off, and the filtrate was evaporated. The residue was 1.32 g (73%) of acid **III**. Its IR and 1H and ^{13}C NMR spectra were identical to those given in [3]. Mass spectrum (NICI), m/z (I_{rel} , %): 363 (3) [$M-H$] $^-$, 344 (100) [$M-HF$] $^-$, 326 (4) [$M-F_2$] $^-$, 300 (11) [$M-HF-CO_2$] $^-$, 262 (2) [$M-HF-CO_2-F_2$] $^-$.

* ^{13}C NMR spectrum of perfluoro-1-alkene (**I**) in $CDCl_3$ - $CF_2ClCFCl_2$, δ_C , ppm (J , Hz): 107.2–123.6 m (CF_2), 118.1 q.t [CF_3 , $^1J(CF) = 287.8$, $^2J(CF) = 32.9$], 121.2 d.t.t [C^2F , $^1J(CF) = 300.3$, $^2J(C-FC^1) = 39.3$, $^2J(C-FC^3) = 34.8$], 156.48 t.d [C^1F_2 , $^1J(CF) = 295.8$, $^2J(CF) = 39.5$].

b. Alkene **I**, 2 g (5 mmol), in 20 ml of Freon-113 was ozonized as described above. The solvent was distilled off, and 10 ml of anhydrous THF was added to the residue. Sodium tetrahydridoborate, 0.38 g (10 mmol), and 10 ml of THF were then added in portions while stirring at room temperature. After 3 h, 5 ml of 2 N hydrochloric acid was added, and the mixture was stirred for an additional 3 h and extracted with ethyl acetate (3 × 20 ml). The extract was dried over MgSO₄ and evaporated to obtain 0.82 g (45%) of acid **III** which was identical (in the IR and ¹H and ¹³C NMR spectra) to a sample prepared as described in *a*.

c. Alkene **I**, 2 g (5 mmol), in 20 ml of Freon-113 containing 0.4 ml (10 mmol) of MeOH was ozonized as described above. The solvent was distilled off to isolate 1.56 g (86%) of acid **III** which was identical (IR, NMR) to a sample prepared as described in *a*.

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-heptanol (IV). *a.* A solution of ozonide **II** in 20 ml of anhydrous THF (prepared from 2 g of alkene **I** by the above procedure) was slowly added (dropwise) with vigorous stirring (argon, 0°C) to a suspension of 0.37 g (9.6 mmol) of LiAlH₄ in 8 ml of anhydrous THF. The mixture was stirred for 4 h at room temperature and was left overnight, 30 ml of 5% hydrochloric acid was slowly added, and the mixture was extracted with Freon-113 (2 × 30 ml). The extract was washed in succession with saturated solutions of NaHCO₃ and NaCl and dried over MgSO₄, and the solvent was removed. Yield of alcohol **IV** 1.57 g (90%). IR spectrum, ν , cm⁻¹: 3350 br.s (OH, $W_{h/2}$ = 342 cm⁻¹). ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 3.96 t [2H, CH₂O, *J*(HF) = 13.2], 4.6 br.s (1H, OH, $W_{h/2}$ = 20 Hz).

b. To a suspension of 0.1 g (2.3 mmol) of LiAlH₄ in 20 ml of THF we added dropwise with stirring (argon, 0°C) a solution of 1.3 g (3 mmol) of acid **III** in 10 ml of THF. The mixture was then treated as described above in *a*. Yield 1.22 g (70%). The product was identical (IR, ¹H NMR) to a sample prepared as described in *a*.

c. To a suspension of 0.18 g (4.7 mmol) of LiAlH₄ in 20 ml of THF we added dropwise with stirring (argon, 0°C) a solution of 1.8 g (4.7 mmol) of ester **VII** or 1.84 g (4.7 mmol) of ester **VIII**. The mixture was then treated as described in *a*. The yield of **IV** was 1.48 g (85%) from ester **VII** or 1.4 g (80%) from ester **VIII**. The product was identical (IR, ¹H NMR) to a sample prepared as described in *a*.

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl acetate (V). A mixture of 0.52 g (1.5 mmol) of

alcohol **IV**, 0.75 ml of acetic anhydride, and 0.8 ml of pyridine was stirred for 72 h. It was then acidified with 5% hydrochloric acid and extracted with diethyl ether (3 × 10 ml). After appropriate treatment, the product was purified by chromatography on silica gel using 3:1 pentane–diethyl ether as eluent. Yield 0.5 g (90%). IR spectrum, ν , cm⁻¹: 1760 s (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 2.16 s (3H, CH₃), 4.59 t [2H, CH₂, ³*J*(HF) = 13.0]. ¹³C NMR spectrum, δ_C , ppm (*J*, Hz): 20.00 s (CH₃), 59.61 t [CH₂, ²*J*(CF) = 27.8], 99.1–136.4 m (CF₂, CF₃), 169.31 s (CO). Found, %: C 24.96; H 1.09. C₈H₅F₁₃O₂. Calculated, %: C 25.28; H 1.33.

Perfluoroheptanamide (VI). To a solution of 1.8 g (5 mmol) of acid **III** in 15 ml of anhydrous methanol we added with stirring 0.7 g (13 mmol) of anhydrous ammonium chloride, and the mixture was kept for 3 days at room temperature. It was then made alkaline by adding a 10% solution of sodium methoxide in methanol and evaporated under reduced pressure (40°C). The residue was extracted with diethyl ether (3 × 20 ml), and the extract was washed with a saturated solution of sodium chloride, dried over MgSO₄, and evaporated. Yield 0.94 g (48%), mp 136°C (decomp.). IR spectrum, ν , cm⁻¹: 1675 s (C=O), 3350 br, s (NH, $W_{h/2}$ = 450 cm⁻¹). ¹H NMR spectrum (CD₃OD), δ , ppm: 5.17 (NH₂, $W_{h/2}$ = 9 Hz). ¹³C NMR spectrum (CD₃OD), δ_C , ppm (*J*, Hz): 104.9–118.1 m (CF₂), 118.6 q.t [CF₃, ¹*J*(CF) = 287.45, ²*J*(CF) = 33.3], 163.5 t [CONH₂, ²*J*(CF) = 31.0]. Mass spectrum (PICI), *m/z* (*I*_{rel}, %): 393 (1) [*M*+C₂H₆]⁺, 379 (17) [*M*+CH₄]⁺, 366 (4), 365 (100) [*M*+H₂]⁺, 347 (11) [*M*-NH₂]⁺, 165 (3), 151 (8), 137 (12), 127 (15), 123 (13), 113 (14), 111 (15), 108 (13), 100 (8). Mass spectrum (NICI), *m/z* (*I*_{rel}, %): 344 (100) [*M*-F]⁻, 328 (74) [*M*-F₂NH₂]⁻, 316 (31) [*M*-F-CO]⁻, 310 (12) [*M*-F₂NH]⁻, 300 (59) [*M*-F₂NH₂-CO]⁻, 290 (27) [*M*-F₂NH-HF]⁻, 262 (46) [*M*-F₂NH-HF-CO]⁻, 224 (11) [*M*-F₂NH-HF-CO-F₂]⁻, 216 (12) [*M*-F-CO-C₂F₄]⁻, 212 (3), 166 (5). Mass spectrum (EI), *m/z* (*I*_{rel}, %): 319 (1) [*M*-CONH₂]⁺, 300 (1) [*M*-CONH₂-F]⁺, 281 (2) [*M*-CONH₂-F₂]⁺, 231 (9) [C₅F₉]⁺, 197 (3), 181 (14) [C₄F₇]⁺, 169 (9), 131 (100) [C₃F₅]⁺, 119 (19), 100 (16) [C₂F₄]⁺, 69 (49) [CF₃]⁺, 45 (51). Found, %: C 22.87; H 0.48; N 3.55. C₇H₂F₁₃NO. Calculated, %: C 23.15; H 0.56; N 3.86.

Methyl perfluoroheptanoate (VII). Alkene **I**, 2 g (5 mmol), in 20 ml of Freon-113 containing 0.8 ml (20 mmol) of methanol was ozonized by the above procedure. Removal of the solvent gave 1.55 g

(82%) of ester **VII**. IR spectrum, ν , cm^{-1} : 1780 s (C=O). ^1H NMR spectrum, δ , ppm (J , Hz): 4.0 s (OCH₃). ^{13}C NMR spectrum, δ_{C} , ppm (J , Hz): 54.1 s (OCH₃), 108.0 t,t [C^2 , $^1J(\text{CF}) = 273$, $^2J(\text{CF}) = 31.9$], 110.5–114.0 m ($\text{C}^3\text{--C}^6$), 117.5 q,t [C^7 , $^1J(\text{CF}) = 278$, $^2J(\text{CF}) = 29$], 159.2 t [C^1 , $^2J(\text{CF}) = 30.0$].

Ethyl perfluoroheptanoate (VIII). Alkene **I**, 2 g (5 mmol), in 20 ml of Freon-113 containing 1.8 ml (30 mmol) of ethanol was ozonized by the above procedure. Removal of the solvent gave 1.47 g (75%) of ester **VIII**. IR spectrum, ν , cm^{-1} : 1780 s (C=O). ^1H NMR spectrum, δ , ppm (J , Hz): 1.39 t (3H, CH₃, $J = 7.1$), 4.45 q (2H, CH₂, $J = 7.1$). ^{13}C NMR spectrum, δ_{C} , ppm (J , Hz): 13.50 s (CH₃), 64.81 s (OCH₂), 96.3–123.8 m ($\text{C}^2\text{--C}^6$), 117.7 q,t [C^7 , $^1J(\text{CF}) = 277$, $^2J(\text{CF}) = 30$], 161.2 t [C^1 , $^2J(\text{CF}) = 29.3$].

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