Synthesis of perfluoroheptanal by ozonolysis of perfluoro-1-octene

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Perfluoro-1-octene was used as a model for developing a method for the preparative ozonolysis of perfluoro-1-alkenes to the corresponding perfluoro-nor-alkenals. Perfluoro-heptanal was synthesized.

Key words: perfluoro-1-octene, ozonolysis; peroxides, reduction; Lindlar catalyst; perfluoroheptanal.

The studies of the ozonolysis of fluorinated olefins have hitherto been confined to the cases of lower perfluoroalkenes.¹⁻⁶ As regards the higher perfluoroolefins (PFO), there are literature data⁷⁻⁹ on the concomitant oxidation of PFO and CF₃COOH during their co-ozonolysis. The corresponding reaction products, perfluoroalkanoyl fluorides, were not isolated, but only identified using ¹⁹F NMR and GLC, the yields being determined by GLC alone.

We have used perfluoro-1-octene (1) as a model for developing a practical method for the ozonolysis of perfluoro- α -olefins. This method consists of ozonizing 1 in freon-113 with subsequent hydrogenation of the resulting peroxides over the Lindlar catalyst. At 80 % conversion the yield of perfluoroheptanal (2) from 1 was as high as 70 %. The structure of aldehyde 2 was confirmed by its ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra. In the IR spectrum of 2 there are absorption bands at 1780 and 2720 cm⁻¹ characteristic of the HCO group in perfluoroaldehydes (see Ref. 10).



Experimental

The IR spectrum was registered on a UR-20 instrument in a film. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer with tetramethylsilane as the internal standard. The ¹⁹F NMR spectrum was obtained on a Tesla BS-567 instrument using CFCl₃ as the internal standard. GLC analysis was performed on a Khrom-5 chromatograph using 5 % SE-30 on Chromaton N-AW-DMCS as the stationary phase and He as the carrier gas. The R_f value of **2** refers to a fixed silica gel layer (Silufol) in hexane/ether 3:1 as the eluent.

Perfluoroheptanal (2). A stream of an ozone/oxygen mixture from an ozonator of 12.5 mmol h⁻¹ capacity was passed at room temperature through a solution of perfluoro-1-octene (1) (2 g, 5 mmol) in freon-113 (20 mL) for 2 h at a rate of 70 mL h^{-1} (25 mmol of O₃). The reaction mixture was then stripped of O_3/O_2 by passing a stream of argon through it. Then 0.02 g of Lindlar catalyst was added and the mixture was stirred at ~20 °C under a hydrogen atmosphere until the complete disappearance of peroxides (as shown by an iodinestarch probe). The catalyst was filtered, the solvent was evaporated and the residue was distilled in vacuo to afford 0.4 g (20 %) of **1** and 1.21 g (70 %) of aldehyde **2**, b.p. 45-46 °C (123 Torr), $n_{\rm D}^{27}$ 1.3119, $R_{\rm f}$ 3.1. IR, v/cm⁻¹: 1100–1400 (C–F), 1780 (C=O), 2720 (C=O). ¹H NMR (CDCl₃), δ : 10.38 (s, 1 H,, CHO). ¹³C NMR (CDCl₃), δ: 104.4-114.7 (m, C(3), C(4), C(5), C(6)); 110.5 (tt, C(2), $J_{C(2)-F} =$ 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).

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The oxidation of alkanols with air oxygen in the catalytic system copper(11) acetate—hydroquinone promoted by visible light

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2-Propanol or 1-propanol in acetonitrile, when exposed to air and irradiated with a tungsten lamp in the presence of catalytic amounts of copper(11) acetate and hydroquinone, are oxidized to give acetone or propanal, respectively.

Key words: photochemistry; propanols, oxidation with air oxygen; copper(II) complexes; metal complex catalysis.

Photoinduced transformations of organic substrates and, particularly, their oxidation in the presence of metal complex catalysts are of great interest as the basis for the synthesis of various organics.¹⁻³ Among them, of special importance are the processes promoted by irradiation in the visible part of the electromagnetic spectrum. Earlier,⁴ the copper(11) acetate-hydroquinone system was shown to catalyze the effective and selective oxidation of alkanes to alkyl hydroperoxides by air oxygen promoted by irradiation with visible light. Complexes of other transition metals (e.g., Fe, Ni, and Co) or copper salts with other anions, such as copper perchlorate, are much less active in this process or even devoid of any catalytic effect. The substitution of resorcinol or pyrocatechol for hydroquinone results in a total loss of photocatalytic activity.

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Here we report our first results obtained in the study of the use of the copper(II) acetate—hydroquinone system as a catalyst for the light-promoted air oxidation of aliphatic alcohols.

Experimental

All experiments were carried out in a cylindrical quartz vessel (1.5 cm in diameter), provided with a water jacket for cooling (to ~15 °C), magnetic stirring bar, and free access to the ambient air. Solutions containing the catalytic system and a substrate (total volume 5 mL) were illuminated with a standard tungsten lamp (100 W) and vigorously stirred. The reaction was monitored by gas chromatography using a DANI 86.10 instrument with a capillary column filled with Carbowax as the stationary phase; 0.1-0.2 mL aliquots were periodically taken out for analysis. The peack areas were measured by means of a Chrom Jet integrator (Spectra Physics). The acetonitrile and the other chemicals used in this work have been purchased from Fluka AG (Switzerland) and used without further purification.

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