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PERFLUORINATED α-OXIDES

I. L. Knunyants, V. V. Shokina, and I. V. Galakhov

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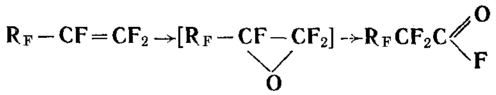
Perfluorinated α-oxides from perfluoropropene, perfluoroisobutene, and 8-hydroperfluorooctene are prepared by oxidizing the perfluoroolefins with alkaline hydrogen peroxide. It is shown that treatment with hydrogen halide acids, alcohols, and thiourea leads to scission of the C–O bond of the α-oxides at the β-carbon atom. The products are α-bromoperfluorocarboxylic acids, esters of α-alkoxyperfluorocarboxylic acids, and 2-amino-4-oxo-5-perfluoroalkylthiazolines.

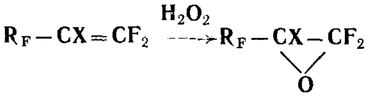
Until recently perfluoro derivatives, and indeed perhalogeno derivatives generally, of α-oxides were regarded as very unstable compounds. The literature [1] contains indications that the oxide of trofluoroethylene is stable only at −80° C. Tetrafluoroethylene [2] isomerizes to give trifluoroacetyl fluoride and partly decomposes to give difluorophosgene.

In a number of cases [3] oxidation of perfluoroolefins gave only fluoroanhydrides of perfluorocarboxylic acids, whose formation can be explained only by isomerization of the intermediate oxide:



In 1963 a patent [4] was published on the preparation of perfluorinated oxides by oxidizing perfluoroolefins with alkaline hydrogen peroxide. The boiling points given for the oxides are practically the same as those of the starting olefins, but the authors do not say anything about the method used for separating them.

We have prepared the oxides of perfluoropropene, ω-hydroperfluorooctene, and perfluoroisobutene by oxidizing the corresponding olefins with alkaline hydrogen peroxide.



$R_F = CF_3$, $X = F$
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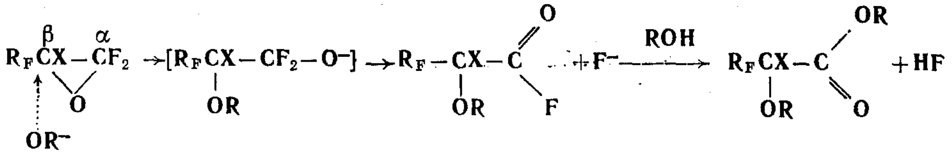
$R_F = H(CF_2)_6$, $X = F$

Addition of the olefin to alkaline hydrogen peroxide, as described in the patent, leads to very vigorous reaction. The reaction can be regulated by slowly adding the olefin, but this greatly reduces the oxide yield. Our experiments showed that after adding olefin, gradual addition of the alkali enables the reaction to be controlled, this being particularly important in preparing perfluoroisobutene oxide, because it is even more toxic than perfluoroisobutene. The oxidation products always contain starting olefin along with the oxide. To obtain the pure oxides of perfluoropropene and ω-hydroperfluorooctene, the oxide-olefin mixtures were brominated, while irradiated with a quartz mercury lamp, when the olefin was converted to dibromide from which the oxide could readily be distilled off.

Separation of perfluoroisobutene oxide from the starting olefin was effected by passing the products through ethanol, when the isobutene instantly reacts to give alkoxyisobutenes.

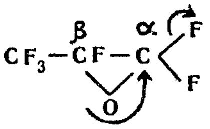
Pure perfluoroisobutene oxide was condensed in a trap. The perfluoro α-oxides are stable, but undergo change when irradiated with a quartz mercury lamp, though they are stable to keeping for a long time or heated at 100° C for a few hr. The IR spectra of perfluoro α-oxides have a characteristic absorption band at 1550 cm^{-1}. When they react with ethanol the C–O bond at the β-carbon atom is broken to give the α-ethoxy esters of the corresponding carboxylic acids.



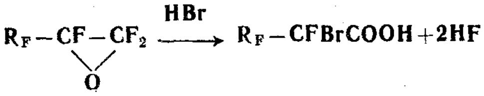
$R = C_2H_5$, CH_3
$R_F = CF_3$, $X = F$
$R_F = CF_3$, $X = CF_3$
$R_F = H(CF_2)_6$, $X = F$

Heating the α-oxide of ω-hydroperfluorooctene and titrating with hydrochloric acid in acetone showed that 3 moles of acid and 2-fluorine ions were present, indicating the same sequence for opening of the oxide ring, at the β-carbon atom.

Apparently, two fluorine atoms are stronger electron acceptors than one fluorine and the fluorinated group, or two fluorinated groups, so that electron density is pulled from the oxygen to the α-carbon atom, which carries two fluorine atoms, bringing about attack of the nucleophilic group at the β-carbon:

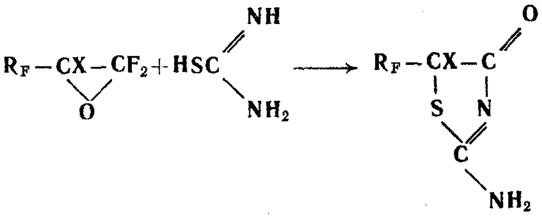


This kind of strengthening effect of powerful electron-accepting groups on the C–O bond has previously [5, 6] been repeatedly observed. Heating perfluoropropene oxide and ω-hydroperfluorooctene oxide with hydrobromic acid at 150° C also results in splitting of the C–O bond at the β-carbon atom, to give α-bromoperfluoropropionic and α-bromo-ω-hydroperfluorocaprylic acids:



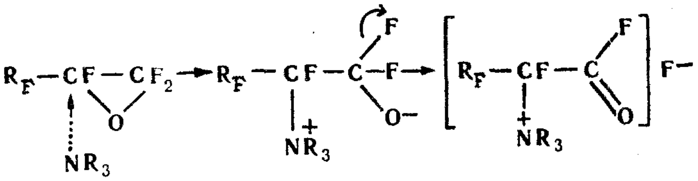
Under such conditions the isobutene oxide is not split by hydrobromic acid.

Of interest was the reaction of perfluorinated α-oxides with thiourea, which led to quantitative yields of the corresponding substituted 2-amino-4-oxothiazolines:

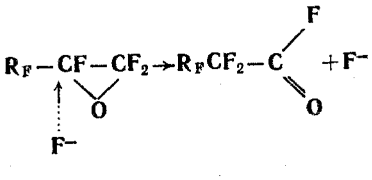


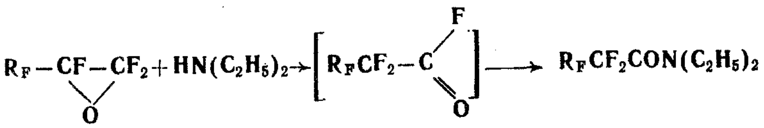
The thiazolines crystallize very well, and can be used to identify perfluorinated α-oxides.

The action of amines on perfluoro α-oxides is found to lead to isomerization to fluoroanhydrides of the corresponding perfluorocarboxylic acids, which react further with the amine to give amides:



followed by





The action of catalytic amounts of triethylamine on perfluoropropene oxide gives the acid fluoride of perfluoropropionic acid, and reaction of the latter with ethanol gives ethyl perfluoropropionate. The action of triethylamine on ω-hydroperfluorocaprylic acid...

Experimental

Perfluoropropene oxide. A mixture of 190 ml MeOH and 130 ml 30% H_2O_2 was cooled to − 50° C, 31 g (about 0.2 mole) perfluoropropene added, and then with good stirring, a solution of 21 g KOH in 40 ml water gradually added. Stirring was continued for 2 hr after all the alkali had been added, the temperature being held at − 40° C, after which the mixture was allowed to warm up to room temperature. The trap condensed 17 g products, comprising 70% perfluoropropene oxide and 30% unoxidized perfluoropropene.

The mixture of oxide and olefin was passed through a quartz test tube containing bromine and irradiated by a quartz mercury lamp, then through a trap cooled with ice, through Na hyposulfite solution, next through $CaCl_2$, and finally into a trap cooled with dry ice and acetone. The oxide was distilled through a podbielniak-type column, bp − 28° C. Yield of I 32% theoretical, based on the reacted perfluoropropene. Found: C 21.54; F 67.54%. Calculated for C_3F_6O: C 21.68; F 68.67%. The IR spectrum has a characteristic absorption band at 1550 cm^{-1}.

Perfluoroisobutene oxide (II). 28 ml 30% H_2O_2 and 100 ml water were mixed, cooled to − 15° C, rapidly stirred, and 30 g (0.15 mole) perfluoroisobutene added, followed by 14 g NaOH in 29 ml water added slowly from a dropping funnel. The reaction products were stirred for 4 hr at − 5° C, and then allowed to warm up to room temperature. Fourteen g liquid condensed in the trap; it was 80% oxide and 15% perfluoroisobutene. It was passed through ethanol to remove the olefin, and distilled, bp 6–7° C. Yield of II 10 g (32% on the isobutene taken). Found: C 22.45; F 70.15%. Calculated for C_4F_8O: C 22.22; F 70.37%. The IR absorption spectrum had the characteristic band at 1550 cm^{-1}.

The aqueous solution was treated with MnO_2 to destroy the remaining H_2O_2, and then repeatedly extracted with ether. After distilling off the ether, 3 g perfluoroacetone hydrate remained, identified as the dianilid.

1, 2, Epoxy-8-hydroperfluorooctane (III). A mixture of 70 ml MeOH and 30 ml 30% H_2O_2 was cooled to −20° C, 23 g (0.06 mole) 8 hydroperfluoro-1, 2-octene added, the whole vigorously stirred and a solution of 8 g KOH in 15 ml water gradually added. When addition was complete, stirring was continued at − 20° C for 2 hr longer. The lower layer was separated off, washed with ice-water, and dried over $MgSO_4$. Product yield 15 g, and gas-liquid chromatography (column: 17% tricresyl phosphate on brick) showed it to contain 80% ω-hydroperfluorooctene oxide. Dry bromine was added to the reaction product until decolorization ceased, then the mixture was washed with Na hyposulfite solution and water, dried over $MgSO_4$, and distilled, to give 12 g (51%) III, bp 118° C; d_4^{20} 1.7389; n_D^{20} 1.2905. Found: C 24.12; H 0.22; F 70.50%; MR_D 41.67. Calculated for $C_8HF_{15}O$: C 24.10; H 0.25; F 71.10%; MR_D 41.41. The absorption spectrum showed the 1550 cm^{-1} band. At the same time there was obtained 3 g 1, 2-dibromo-8-hydroperfluorooctane, bp 188° C; d_4^{20} 20851; n_D^{20} 1.3530. Found: C 18.10; H 0.17; F 52.80; Br 29.44%; MR_D 56.36. Calculated for $C_8HF_{15}BR_{12}$: C 17.8; H 0.18; F 52.50; Br 29.5%; MR_D 56.58.

Ethyl α-ethoxyperfluoropropionate (IV). 6 g (~0.036 mole) I and 8 ml dry EtOH were sealed together in a pressure tube and left for 3 days at room temperature. Then the contents were poured on to ice, the lower layer separated off, washed with water, $NaHCO_3$ solution, and then with water again, after which it was dried over $MgSO_4$ and distilled, to give 5 g (63%) IV, bp 138° C; d_4^{20} 1.227; n_D^{20} 1.3482. Found: C 38.58; H 4.63; F 35.35%; MR 38.05. Calculated for $C_7H_{10}F_4O_3$: C 38.53; H 4.58; F 34.86%. MR 38.19.

Treatment with aqueous ammonia gave α-ethoxyperfluoropropionamide mp 83° C (ex water). Found: F 40.41; N 7.54%. Calculated for $C_5H_7F_4O_2N$: F 40.21; N 7.41%.

Ethyl α-ethoxyperfluoroisobutyrate (V). Prepared similarly to the above by keeping together in a sealed tube 6 g (~0.028 mole) II and 6 ml dry EtOH at room temperature for 2 days. The product was worked up in the same way. Yield of V 4.6 g (67%), bp 73° (60 mm); d_4^{20} 1.327; n_D^{20} 1.3400. Found: C 35.78, 35.87; H 3.62, 3.85; F 44.54, 44.45%; MR 42.23. Calculated for $C_8H_{10}F_6O_3$: C 35.83; H 3.73; F 42.54; MR 42.99.

Methyl-α-methoxyperfluoroisobutyrate was prepared similarly from MeOH and perfluoroisobutene oxide, bp 119°C; d_4^{20} 1.456; n_D^{20} 1.3290. Found: C 29.40; H 2.32; F 47.35%; MR 33.54. Calculated for $C_6H_6F_6O_3$: C 30.00; H 2.5; F 47.5%; MR 33.75.

Ethyl α-ethoxy-ω-hydroperfluorocaprylic acid (VI). 4g (~0.01 mole) III and 8 ml dry EtOH were refluxed together for 2 hr, and after cooling the products poured onto ice, the lower layer separated off, washed with water, then with $NaHCO_3$ solution, and finally with water again. Then it was dried over $MgSO_4$ and distilled, to give 3.7 g (90%) VI, bp 142° C (45 mm); d_4^{20} 1.5340; n_D^{20} 1.3430. Found: C 31.8; H 2.48; F 53.61%; MR 62.1. Calculated for $C_{12}H_{11}F_{13}O_3$: C 32.00; H 2.44; F 54.89%; MR 61.98.

α-Bromoperfluoropropionic acid (VII). 7 g (~0.042 mole) I and 10 ml HBr (d 1.42) were put in a glass pressure tube, which was inserted in its steel protective jacket, and heated for 4 hr at 120° C. The lower layer was separated off, washed with water, dried over $MgSO_4$, and distilled, yield of VII 7 g (74%), bp 60° C (22 mm); d_4^{20} 1.936; n_D^{20} 1.3711. Found: C 15.45; H 0.82; F 32.38; Br 37.01%; MR 26.35, neutralization equivalent 220. Calculated for $C_3HF_4BrO_2$: C 16.00; H 0.45; F 33.78; Br 35.56%; MR 25.83, neutralization equivalent 225.

α-Bromo-ω-hydroperfluorocaprylic acid (VIII). 4 g (~0.01 mole) III 6 ml HBr and 2 ml acetone were refluxed together for 10 hr, the products poured on to ice, extracted with ether, and, the ether extracts dried over $MgSO_4$. After distilling off the ether, the residue was vacuum-distilled, to give 2.6 g (57%) VIII, bp 126° C (13 mm), which crystallized but which was very hygroscopic. Found: C 21.77; H 0.75; F 52.58%. Calculated for $C_8H_2F_{13}O_2Br$: C 21.01; H 0.45; F 54.05; Br 17.5%.

N,N-diethylperfluoropropionamide (IX). 5 g (0.03 mole) I was passed into a solution of 6 g (~0.082 mole) diethylamine in 15 ml dry ether cooled in ice. The precipitate of diethylamide hydrofluoride was filtered off and washed with dry ether. The ether solution was washed with water, dried over $MgSO_4$, and distilled, to give 5 g (75.7%) IX, bp 84° C (57 mm); d_4^{20} 1.254; n_D^{20} 1.3622. Found: C 38.36, 38.50; H 4.21, 4.54; F 43.47, 43.60%; MR 38.76. Calculated for $C_7H_{10}F_5NO$: C 38.36; H 4.56; F 43.38%; MR 38.81.

N,N-diethylperfluorobutyramide (X). This was prepared similarly, by treating II with diethylamine, yield 68%, bp 85° C (55 mm); d_4^{20} 1.337; n_D^{20} 1.3548. Found: C 35.67; H 3.86; F 49.43; N 5.62%; MR 43.83. Calculated for $C_8H_{10}F_7NO$: C 35.69; H 3.72; F 49.45; N 5.21%; MR 43.68.

N,N-diethyl-ω-hydroperfluorocaprylamine (XI). 1.5 g (~0.02 mole) diethylamine in 5 ml dry ether was added to 4 g (~0.01 mole) III in 10 ml dry ether. The precipitate of diethylamide hydrofluoride was filtered off, the ether solution washed with water, then with dilute HCl, and again with water, then dried over $MgSO_4$. The residue obtained after distilling off the ether was vacuum-distilled, to give 2.2 g (50%) XI, bp 86–90° C (0.1 mm); d_4^{20} 1.578; n_D^{20} 1.3560. Found: C 31.51; H 2.61; F 58.19; N 3.08%; MR 62.45. Calculated for $C_{12}H_{11}F_{14}ON$: C 31.93; H 2.44; F 58.98; N 3.11%; MR 62.72.

Ethyl perfluoropropionate (XII). 4 g (~0.024 mole) I and 2 drops of Et_3N were sealed together in a pressure tube, and left for 2 days at room temperature. Then the contents were passed through 10 ml dry EtOH cooled in ice, and the products poured onto ice. The layer which was separated was washed with water, then with $NaHCO_3$ solution, and finally with water again, then dried over $MgSO_4$. Distillation gave 3 g (65%) XII, bp 73° C (722 mm); n_D^{20} 1.3010. The literature [7] gives 76° C (773 mm); n_D^{20} 1.300. The amide ex ether has mp 95° C, the same as that given in [7] for the amide of perfluoropropionic acid.

ω-Hydroperfluorocaprylyl fluoride (XIII). 3 drops of Et_3N were added to 6 g (~0.015 mole) III, the mixture heated to 40° C under reflux, and then distilled, to give 5 g (83%) XIII, bp 120° C; n_D^{20} 1.2910. The IR absorption spectrum had a characteristic band at 1880 cm^{-1}. Titration of 0.0746 g used 3.85 ml 0.1 N KOH, neutralization equivalent 388. Found: C 23.95; H 0.17; F 71.27%. Calculated for $C_8HF_{15}O$: C 24.12; H 0.25; F 71.61%, neutralization equivalent 398. The acid fluoride is quickly hydrolyzed in air.

ω-Hydroperfluorocaprylic acid. Hydrolysis of the acid fluoride with water gave ω-hydroperfluorocaprylic acid, mp 41° C (ex toluene). It crystallizes with one molecule of water which it loses on standing in a vacuum-desiccator over P_2O_5, but in air the water is rapidly regained. Found: C 23.21; H 0.99; F 64.15%, neutralization equivalent 415 (titration with ethanolic alkali, using phenolphthalein). Calculated for $C_8H_4F_{14}O_3$: C 23.19; H 0.97; F 64.25%, neutralization equivalent 414.

The anilide had mp 107–108° C (ex benzene), soluble in ether. Found: N 2.90%. Calculated for $C_{14}H_9F_{14}O_2N$: N 2.86%.

2-Amino-4-oxo-5-perfluoromethylthiazoline (XIV). A flask was fitted with a stirrer, reflux condenser, and gas inlet tube, and cooled with dry ice-acetone. It was charged with 2 g thiourea in 25 ml EtOH, this was cooled to −30° C, vigorously stirred, and 2 g (0.012 mole) I condensed in it, after which stirring was continued for 3 hr while gradually warming up to room temperature. The products were diluted with 25 ml water and the precipitate filtered off, washed with water, toluene (to remove S), and recrystallized from aqueous MeOH. Yield of XIV quantitative, mp 190–192° C (decomp). Found: C 24.38; H 1.05; F 38.07; N 13.95%. Calculated for $C_4H_2F_4N_2SO$: C 23.76; H 0.99; F 37.62; N 13.86%.

2-Amino-4-oxo-5-ω-hydroperfluorohexylthiazoline (XV). 2 g (~0.005 mole) III was added to a stirred solution of 0.4 g thiourea in 10 ml MeOH. Then stirring was continued for 3 hr longer at room temperature, and a precipitate appeared. The products were diluted with 2 volumes of water, the precipitate filtered off, washed with water and toluene (to remove S). XV was obtained in quantitative yield, mp 205° C (ex aqueous MeOH). Found: C 24.54; H 0.63; F 56.75; N 6.5%. Calculated for $C_9H_3F_{13}N_2SO$: C 24.80; H 0.69; F 56.80; N 6.46%.

2-Amino-4-oxo-5, 5-difluoromethylthiazoline (XVI). 2 g (~0.005 mole) II was condensed in a solution of 1 g thiourea in 15 ml MeOH which was stirred and cooled. The mixture was stirred for 2 hr at room temperature, using a dry ice condenser. The solution was filtered to remove S formed, the filtrate diluted with 2 volumes of water, and the precipitate filtered off. Yield of SVI 0.7 g (56%), mp 240° C (decomp, ex aqueous EtOH). Found: N 11.49, 11.23; F 44.41, 44.71%. Calculated for $C_5H_2F_6N_2SO$: N 11.11; F 45.24%

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Institute of Heteroorganic Compounds
AS USSR, Moscow