OXIDATIVE CONDENSATION OF MONO- AND DIHYDROPERFLUOROALKANES

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According to Germain et al. [1], the oxidative fluorosulfatization of 1-hydroperfluoroalkanes upon electrolysis in FSO_2OH, which proceeds through a free radical mechanism, leads to the formation of perfluoroalkyl fluorosulfates as the only reaction products.

We have established that the fluorosulfatization of hydroperfluoroalkanes upon their electrolysis in FSO_2OH under conditions when their concentration exceeds the current concentration of peroxydisulfuryl difluoride is accompanied by oxidative dehydrodimerization. Thus, perfluorohexadecane (III) is formed in the electrolysis of $C_8F_{17}H$ (I) in FSO_2OH, while α,ω-bis(fluorosulfato)perfluorohexadecane (VI) is formed in the electrolysis of $H(CF_2)_8H$ (IV).

$$\underset{(I)}{C_8F_{17}H} \xrightarrow[\text{electrolysis (3F)}]{HSO_3F} \underset{(II)}{C_8F_{17}OSO_2F} + \underset{(III)}{C_{16}F_{34}}$$

$$\underset{(IV)}{H(CF_2)_8H} \xrightarrow[\text{electrolysis (6F)}]{HSO_3F} \underset{(V)}{FSO_2O(CF_2)_8OSO_2F} + \underset{(VI)}{FSO_2O(CF_2)_{16}OSO_2F}$$

This reaction is the first example of the oxidative dehydrodimerization of hydroperfluoroalkanes. A mixture of 21 g (50 mmoles) (I) and 40 ml HSO_3F, containing 3 g $NaSO_3F$, was subjected to electrolysis in a diaphragmless cell with a vitreous carbon anode and titanium cathode for 20 h at 0.2 A. Treatment of the reaction mixture gave 18.4 g (71%) (II), bp 156-157°C and 2.8 g (14%) (III), mp 124-125°C (125-126°C [2]). Found: C, 18.50; H, 66.02%. Calculated for $C_8F_{18}SO_3$: C, 18.53; F, 66.02%. Under analogous conditions, 20 g (50 mmoles) (IV) upon electrolysis at 0.2 A over 40 h gave 17.5 g (58%) (V), bp 89-92°C (11 mm) (90-93°C (10 mm [3])) and 6.1 g (24%) (VI), bp 134-137°C (3 mm). Found: C, 19.08; S, 6.52%. Calculated for $C_{18}F_{34}O_6S$: C, 19.20; S, 6.40%.

LITERATURE CITED

1. A. Germain, D. Brunel, and P. Moreau, Bull. Soc. Chim. France, No. 6, 895 (1986).
2. R. N. Haszeldine and F. Smith, J. Chem. Soc., 3617 (1950).
3. German Federal Republic Patent No. DE 3,128,113 A1 (1983).

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