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LETTERS TO THE EDITOR

Decomposition of Polyfluoroalkyl Chlorosulfites in the Presence of Copper(I) Chloride

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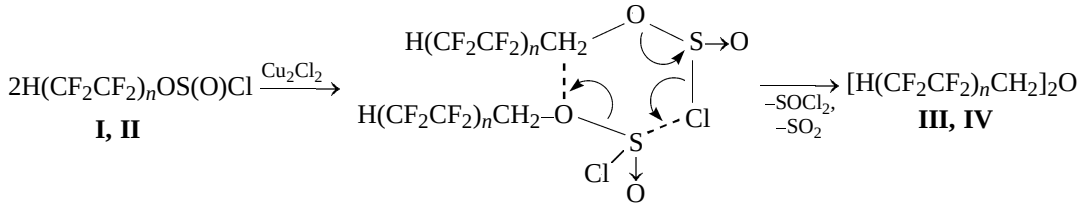
Alkyl chlorosulfites are formed as intermediates in reactions of thionyl chloride with alcohols and are readily converted into chloroalkanes. Polyfluoroalkyl chlorosulfites can be distilled under reduced pressure without decomposition [1]. On heating to ~100°C, these compounds, like nonfluorinated alkyl chlorosulfites, lose sulfur dioxide to give polyfluorochloroalkanes [2].

We have found that copper(I) chloride changes the reaction direction so that decomposition of polyfluoroalkyl chlorosulfites leads to formation of bis(polyfluoroalkyl) ethers. Presumably, the reaction involves intermediate formation of a six-membered cyclic complex.



n = 1 (**I, III**), 2 (**II, IV**).

The reactions were carried out in hexane and 1-hexene. The yield of ether **III** in 1-hexene was 63%, and it decreased to 55% in the case of compound **IV**. The lower yield of **IV** is likely to be determined by greater steric hindrances to complex formation with the substrate having a longer perfluorinated carbon chain. The yield of ether **IV** in hexane was 33%.

1,1,2,2-Tetrafluoro-3-(2,2,3,3-tetrafluoropropoxy)propane (III). Chlorosulfite **I**, 7.1 g, was added at –10°C to a suspension of 1.63 g of copper(I) chloride in 21 ml of 1-hexene. The mixture was then heated to 55°C and was kept for 2 h at that temperature. The coppersalt was filtered, the solvent was distilled off from the filtrate, and the residue was distilled under reduced pressure. Yield 2.6 g (63%), bp 65°C (1 mm Hg), n_D^{20} = 1.3570, d_4^{20} = 1.6270; published data [3]: bp 65°C (1 mm Hg), n_D^{20} = 1.3575, d_4^{20} = 1.6251.

1,1,2,2,3,3,4,4-Octafluoro-5-(2,2,3,3,4,4,5,5-ocktafluoropentoxy)pentane (IV) was synthesized in a similar way using 1.14 g of copper(I) chloride, 16 ml of 1-hexene, and 7.23 g of chlorosulfite **II**. Yield 2.82 g (55%), bp 115°C (4 mm), n_D^{20} = 1.3401, d_4^{20} = 1.7301; published data [3]: bp 103°C (2 mm), n_D^{20} = 1.3385, d_4^{20} = 1.7344.

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