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LETTERS TO THE EDITOR

New Synthesis of Polyfluoroalkyl Cyclohexyl Ethers

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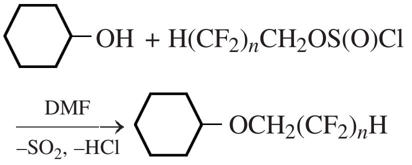
Polyfluorinated cyclohexyl ethers were previously prepared by hydrogenation of mixtures of polyfluorinated alcohols and ketones under pressure over a palladium catalyst [1].

We found that, unlike secondary aliphatic alcohols which do not react with polyfluoroalkyl chlorosulfites, cyclohexanol reacts with these compounds under DMF catalysis to form cyclohexyl ethers in 65–82% yields depending on the size of the perfluorocarbon chain in the alkyl chlorosulfite.



I, II, III

$n = 2$ (**I**); $n = 4$ (**II**); $n = 6$ (**III**).

The yield of the target product decreases in the order $n = 2 > n = 4 > n = 6$. The resulting ethers are transparent liquids readily distillable in a vacuum and possessing a specific odor.

The structure of the synthesized polufluoroalkyl cyclohexyl ethers was established by means of IR and ^1H NMR spectroscopy. IR spectrum, ν, cm^{-1}: 1170 m [ν(C–O–C)], 1170 s [ν(CF_2)], 2878 m, 2965 m [ν(CH_2)], 3005 w (CHF_2). The IR spectra were recorded on a Specord M-82 spectrometer in thin layer on KBr plates. ^1H NMR spectrum, δ, ppm: 5.99 t.t (HCF_2), 3.95 t (CH_2CF_2), 2.89 m (ring CH), 1.75 m and 1.31 m (ring CH_2). The ^1H NMR spectra were taken on a Varian Mercury Plus spectrometer (300 MHz) in $CDCl_3$ against internal TMS.

(1,1,3-Trihydroperfluoropropoxy)cyclohexane (I). A solution of 2.3 g of cyclohexanol and 0.015 ml of DMF in 10 ml of chloroform was cooled to –10°C, and a solution of 4.93 g of 1,1,3-trihydroperfluoropropyl chlorosulfite in 10 ml of chloroform was added with stirring at this temperature. The reaction mixture was then heated to 25°C and kept for 3 h. The liberating hydrogen chloride and sulfur dioxide were removed with stream of dry air. The solvent was evaporated, and the residue was distilled in a vacuum to give 4.03 g (82%) of the target ether, bp 95°C (3 mm Hg), n_D^{20} 1.3798, d_4^{20} 1.1005. Found F, %: 32.20, calculated F, %: 35.48.

(1,1,5-Trihydroperfluoropentoxy)cyclohexane (II) was prepared in a similar way from 2.5 g of cyclohexanol, 7.9 g of 1,1,5-trihydroperfluoropentyl chlorosulfite, and 0.0016 ml of DMF. Yield 5.9 g (75%), bp 105°C (3 mm Hg), n_D^{20} 1.3865, d_4^{20} 1.3733. Found F, %: 49.61; calculated F, %: 48.37.

(1,1,7-Trihydroperfluoroheptyloxy)cyclohexane (III) was prepared in a similar way from 2.6 g of cyclohexanol, 10.77 g of 1,1,7-trihydroperfluoroheptyl chlorosulfite, and 0.0016 ml of DMF. Yield 7.0 g (65%), bp 123°C (3 mm Hg), n_D^{20} 1.3891, d_4^{20} 1.4067. Found F, %: 54.12; calculated F, %: 55.04.

REFERENCES

1. US Patent 6060626, *Chem. Abstr.,* 2002, no. 09/05744.