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LETTERS TO THE EDITOR

A New Method for Preparing Polyfluorinated Ethers

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Polyfluorinated ethers are prepared by various methods described in detail in [1–3]. We have developed a new method based on reactions of saturated monohydric alcohols and phenol with polyfluoroalkyl chlorosulfinates in the presence of tertiary amines. Alcohols and phenol were taken as complexes with an equimolar amount of triethylamine:

$$\mathrm{ROH{\cdots}NEt_3 + R_FCH_2OS(O)Cl}$$
$$\longrightarrow \underset{\textbf{I–V}}{\mathrm{ROCH_2R_F}} + \mathrm{SO_2} + \mathrm{Et_3N\cdot HCl},$$

R = Pr (**I**), Bu (**II**), n-C_5H_{11} (**III**), R_F (**IV**), Ph (**V**); R_F = HCF_2CF_2 (**a**), $H(CF_2CF_2)_2$ (**b**).

A solution of polyfluoroalkyl chlorosulfinate was added at a temperature from –10 to –5°C to a complex of an alcohol (or phenol) with triethylamine, prepared in advance, after which the reaction mixture was allowed to stand for 5–6 h at room temperature (solvent pentane or hexane). The resulting salt, triethylammonium chloride, is insoluble in this solvent and immediately precipitates. The resulting ether was purified by vacuum distillation; yield 39–51%. The alcohols and phenol should be thoroughly dried before the reaction, since polyfluoroalkyl chlorosulfinates are readily hydrolyzed.

The structure of the resulting ethers was proved by IR spectroscopy and hydrolysis. For the known compounds (**Va**, **Vb**), the constants were compared with the published data.

1,1,5-Trihydroperfluoropentoxypropane Ib. A 1.4-g portion of propanol was mixed with 2.5 g of triethylamine in 20 ml of pentane, and the solution was cooled to –5°C. A solution of 7.7 g of 1,1,5-trihydroperfluoropentyl chlorosulfinate in 15 ml of pentane was added in portions, so as to maintain the temperature within the range from –5 to –10°C. After mixing the reactants, the mixture was allowed to warm up to 20°C and was kept at this temperature for 5 h. The precipitate of triethylammonium chloride was filtered off, the solvent was distilled off, and the product was vacuum-distilled. Yield of **Ib** 2.8 g (42%), bp 104°C (13 mm Hg), n_D^{20} 1.3705, d_4^{20} 1.4234, MR_D 43.59, calculated 41.98. IR spectrum, ν, cm^{-1}: 1154 (COC), 1180 (CF_2), 2892 (CH_2O), 2980 (CH_2, CH_3). Compounds **II**–**V** were prepared similarly.

1,1,3-Trihydroperfluoropropoxybutane IIa. Yield 45%, bp 102°C (4 mm Hg), n_D^{20} 1.3700, d_4^{20} 1.4165, MR_D 45.99, calculated 46.63. IR spectrum, ν, cm^{-1}: 1171 (COC), 1206 (CF_2), 2912 (OCH_2), 2963 (CH_2), 2997 (CH_3).

1,1,3-Trihydroperfluoropropoxypentane IIIa. Yield 49%, bp 88°C (2 mm Hg), n_D^{20} 1.3996, d_4^{20} 1.0371, MR_D 47.18, calculated 41.49. IR spectrum, ν, cm^{-1}: 1137 (COC), 1214 (CF_2), 2885 (OCH_2), 2963 (CH_2, CH_3).

Bis(1,1,5-trihydroperfluoropentyl) ether IVb. Yield 39%, bp 138°C (16 mm Hg), n_D^{20} 1.3385, d_4^{20} 1.7344, MR_D 53.69, calculated 52.27. IR spectrum, ν, cm^{-1}: 1137 (COC), 1176 (CF_2), 2928 (CH_2).

1-Phenoxy-1,1,3-trihydroperfluoropropane Va. Yield 43%, bp 53°C (3 mm Hg), n_D^{20} 1.4508, d_4^{20} 1.4378 (published data: mp 186°C, n_D^{20} 1.4388, d_4^{20} 1.8992 [2]), MR_D 38.94, calculated 42.59. IR spectrum, ν, cm^{-1}: 2932 (CH_2), 1604, 1504 (Ph), 1239, 1032 (COC), 1192 (CF_2).

1-Phenoxy-1,1,5-trihydroperfluoropentane Vb. Yield 51%, bp 68°C (3 mm Hg), n_D^{20} 1.3980, d_4^{20} 1.5760 {published data: bp 85–86°C (4.5–5 mm), n_D^{20} 1.4060, d_4^{20} 1.4587 [2]}, MR_D 47.48, calculated 52.37. IR spectrum, ν, cm^{-1}: 2932 (CH_2), 1604, 1504 (Ph), 1239, 1032 (COC), 1192 (CF_2).

The IR spectra were recorded on a Specord M-82 spectrophotometer (thin films).

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