Russian Journal of Organic Chemistry, Vol. 39, No. 6, 2003, p. 900. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 6, 2003, p. 949.

SHORT COMMUNICATIONS

O-Polyfluoroalkylation of Phenol with Polyfluoroalkyl Chlorosulfites

A. I. Rakhimov, A. V. Nalesnaya, and O. V. Vostrikova

Volgograd State Technical University, Volgograd, Russia
Institute of Chemical Problems of Ecology, Volgograd, 400066 Russia

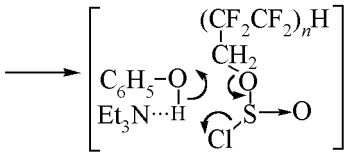
Received November 6, 2002

Polyfluoroalkyl phenyl ethers were previously prepared by a reaction of bromobenzene with alcoholates of polyfluorinated alcohols in pyridine in the presence of copper [1]. No published reports on synthesis of polyfluoroalkyl phenyl ethers by direct polyfluoroalkylation of phenol were found.

We established that polyfluoroalkyl chlorosulfites **I, II** react with a complex of phenol with triethylamine furnishing polyfluoroalkyl ethers of phenol. The reaction is likely to occur via six-membered transition state. Besides polyfluoroalkyl phenyl ethers **III** and **IV** form also SO_2 and triethylamine hydrochloride.

$$C_6H_5OH\cdots NEt_3 + H(CF_2CF_2)_nCH_2OS(O)Cl$$

I, II



$$\longrightarrow C_6H_5OCH_2(CF_2CF_2)_nH$$

III, IV

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

The structure of ethers obtained was confirmed by IR spectra and hydrolysis. The acid hydrolysis of the ethers gives rise to phenol and trihydroperfluoroalkanol.

1-Phenoxy-1,1,3-trihydroperfluoropropane (III). With 3.71 g (0.04 mol) of triethylamine was mixed 3.45 g (0.04 mol) of phenol till complete dissolution, the mixture was diluted with 15 ml of pentane, cooled to −10°C, and at this temperature while stirring was added a solution of 7.87 g (0.04 mol) of polyfluoroalkyl chlorosulfite (**I**) in 20 ml of pentane maintaining the temperature at the same level. The reaction mixture was left standing at room temperature for 24 h. The triethylamine hydrochloride was filtered off, the pentane was distilled off, and the product was distilled in a vacuum. Yield of ether **III** 3.24 g, 42.5 %, bp 53–54°C (p 3 mm Hg), n_D^{20} 1.4508, d_4^{20} 1.4378. Similarly from 2.51 g (0.03 mol) of phenol, 2.70 g (0.03 mol) of triethylamine, and 8.4 f (0.03 mol) of polyfluoroalkyl chlorosulfite (**II**) was prepared ether **IV.** Yield 4.29 g (51%), bp 68–75°C (p 3 mm Hg), n_D^{20} 1.3980, d_4^{20} 1.5762.

IR spectra of phenol ethers obtained were recorded on spectrometer Specord-M82 from thin films. The following absorption bands were present (cm^{-1}): 2932, stretching vibrations of a methylene group; 1604 and 1504, stretching vibrations of the aromatic ring; 1239, asymmetric stretching vibration of the C–O–C bond, 1032, symmetric stretching vibration of the C–O–C bond, 1192, stretching vibrations of CF_2 groups.

REFERENCES

1. Shelud'ko, E.V. and Kalibabchuk, I.I., *Zh. Org. Khim.*, 1979, vol. 15, p. 1661; Shelud'ko, E.V., *Dokl. Akad. Nauk SSSR*, 1978, p. 1008.

1070-4280/03/3906-0900$25.00 © 2003 MAIK "Nauka/Interperiodica"