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LETTERS TO THE EDITOR

Features of Reaction of Polyfluoroalkyl Chlorosulfites with Salicylaldehyde

A. I. Rakhimov*, A. S. Babushkin*, A. V. Nalesnaya, and O. V. Vostrikova***

* *Volgograd State Technical University, Volgograd, Russia*
** *Institute of Chemical Problems of Ecology, Russian Academy of Natural Sciences, Volgograd, Russia*

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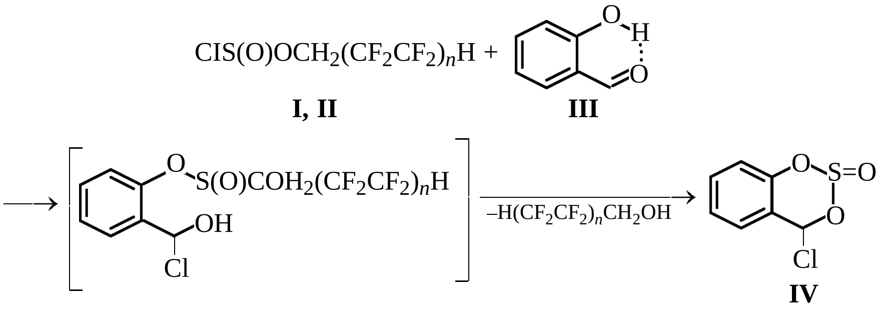
It is known [1] that phenol reacts with polyfluoroalkyl chlorosulfite gives rise to polyfluroalkyl phenyl sulfites. However, we failed to isolate polyfluoroalkyl esters in the reactions of polyfluoroalkyl chlorosulfites **I** and **II** with salicylaldehyde (**III**). The major reaction products were cyclic sulfite **IV** and a polyfluorinated alcohol (see scheme).



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

The reactions were performed in the presence of triethylamine [1, 2], with a DMF catalyst [3] or with no catalyst, using equimolar reagent amounts and hexane as solvent. The catalyst was found to have no effect of the reaction direction, and sulfite **IV** is formed in ~57% yield. The presence of an intramolecular hydrogen bond in aldehyde **III** favors the first stage of nucleophilic substitution and formation of 2-(chlorohydroxymethyl)phenyl polyfluoroalkyl sulfite that further cyclizes into sulfite **IV**.

The IR spectrum of compound **IV** lack HO and >C=O stretching absorption bands and contains bands characteristic of the aromatic ring (1600 cm^{-1}), as well as >S=O (1220 c^{-1}, s), C–O (952 cm^{-1}, s), and S–O (756 cm^{-1}, s) stretching vibration bands [4]. The ^{1}H NMR spectrum of sulfite **IV** lack the triplet of triplets near 5.9 ppm, characteristic of the HCF$_2$CF$_2$ group, but contains a multiplet near 7.08–7.16 ppm from four aromatic protons. The singlet at 6.15 ppm is associated with the cyclic >CH–Cl proton.

4-Chloro-4*H*-5,6-benzo-1,3,2λ^4-dioxathiine 2-oxide (IV). To a solution of 4.78 g of aldehyde **III** in hexane (1 : 3) at 10–15°C we added 8.4 g of 1,1,3-trihydroperfluoropropyl chlorosulfite (**I**) in hexane. The reaction mixture was heated for 6 h at 50°C under dry air and then the solvent and aldehyde **III** (3.68 g) were distilled off. The residue was cooled to 6°C to obtain a precipitate whose recrystallization from chloroform gave 1.2 g (57%) of sulfite **IV** as colorless crystals, mp 131–131.5°C. Found, %: Cl 16.0; S 14.6. $C_7H_5ClO_3S$. Calculated, %: Cl 17.2; S 15.5.

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The IR spectra were obtained on a Specord M-82 instrument in mineral oil. The ^{1}H NMR spectra were measured on a Varian Mercury-300 instrument (300 MHz), internal reference TMS, solvent CCl_4.

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