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LETTERS TO THE EDITOR

New Catalytic Synthesis of Polyfluoroalkyl Chlorosulfites

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Polyfluoroalkyl chlorosulfites are most commonly synthesized by reactions of polyfluoroalkylated alcohols with thionyl chloride in the presence of triethylamine as hydrogen chloride acceptor [1, 2]. The known procedure involves removal of the triethylammonium chloride formed and subsequent regeneration of triethylamine. Furthermore, the yields of polyfluoroalkyl chlorosulfites by this procedure are rather low and the products are unstable when handled.

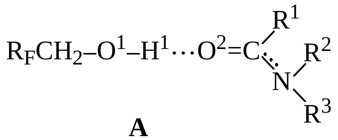
We found that reactions of polyfluoroalkylated alcohols with thionyl chloride, catalyzed by primary, secondary, and tertiary amides of aliphatic and aromatic acids **I**–**VII**, form polyfluoroalkyl chlorosulfites in 72–90% yields. The reactions are performed at an alcohol:thionyl chloride: catalyst **I**–**VII** molar ratio of 1 : (1.5–2) : (0.001–0.01) in two stages. In the first stage, a solution of catalyst **I**–**VII** in a polyfluorinated alcohol is added to a cold (–15 to –10°C) thionyl chloride and in the second, the temperature of the reaction mixture is raised to 25–30°C to remove the hydrogen chloride formed.

$$SOCl_2 + H(CF_2CF_2)_nCH_2OH \xrightarrow{\overset{R^1C(O)NR^2R^3}{\mathbf{I{-}VII}}} H(CF_2CF_2)_nCH_2OS(O)Cl + HCl,$$

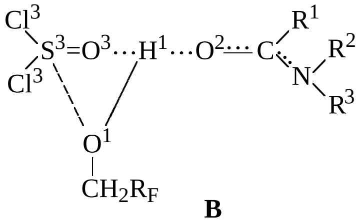
n = 1–3; $R^1 = R^2 = H$, $R^3 = Ph$ (**I**); $R^1 = H$, $R^2 = R^3 = Ph$ (**II**); $R^1 = H$, $R^2 = R^3 = Me$ (**III**); $R^1 = Ph$, $R^2 = R^3 = H$ (**IV**); $R^1 = Ph$, $R^2 = R^3 = Me$ (**V**); $R^1 = R^2 = R^3 = Me$ (**VI**); $R^1 = Me$, $R^2 = R^3 = Et$ (**VII**).

The lowest yields of polyfluoroalkyl chlorosulfites are observed with benzamide (**IV**), *N*,*N*-diphenylformamide (**II**), and formanilide (**I**): 72, 80, and 80 %, respectively. The highest yields (85–90%) were obtained with *N*,*N*-dimethyl(or diethyl)amides of formic (**III**), acetic (**VI**, **VII**), and benzoic (**V**) acids.

We performed an AM1 quantum-chemical analysis [3, 4] of the possible mechanism of catalysis of the reaction of fluorinated alcohols with $SOCl_2$, leading to polyfluoroalkyl chlorosulfites. As the reaction coordinate we chose the H^1–O^1 bond of the alcohol, whose length was set constant in each point of the energetic curve, and all other parameters were optimized. In the initial solution, the catalyst associates with the polyfluorinated alcohol (associate **A**), and the energy gain in associate **A** is 0.352 eV compared with the nonassociated parent compounds. Therewith, the charge on O^2 varies from –0.35 in isolated *N*,*N*-dimethylformamide (compound **III**) to –0.40 in the associate. The charge on H^1 in the alcohol increases from +0.22 to +0.23. Upon addition of the alcohol solution into excess $SOCl_2$, a new associate **B** is formed, in which the alcohol OH proton is simultaneously associated with the amide and thionyl chloride oxygens.



A



B

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The energy gain for complex **B** is 0.553 eV. It is stabilized by the p–π conjugation of the lone electron pair of the amide nitrogen. This changes bond orders and atomic charges. As H^1 moves away from O^1 at a distance of 1.500 Å (the H^1–O^1 distance in the parent alcohol molecule is 0.977 Å), the bond orders change in the following way: $p(H^1–O^1)$ decreases from 0.9117 to 0.1717, $p(H^1–O^2)$ increases from 0.0095 to 0.6529, and $p(O^1–S^3)$ increases from 0.0003 to 0.3576 [$R(O^1–S^3)$ is 1.904 Å]. The atomic charges in complex **B** change as follows: $q(H^1)$ increases to 0.36, $q(O^2)$, to –0.59, and $q(S^3)$, from 0.95 to 1.16, and $q(Cl^3)$ is –0.41. This favors nucleophilic attack of sulfur on the negatively charged R_FCH_2O group.

For the final stage of the nucleophilic substitution of halogen by the polyfluoroalkoxy group, we simulated torsion of the chlorine atom and HCl formation. As the reaction coordinate we chose the H^1–Cl^3 bond which was decreased from 4.212 Å to the covalent bond length 1.3 Å at 0.1 Å steps. This process is characterized by two low barriers: the first, at the reaction coordinate 3.0 Å, is 0.135 eV and is formed by complete H^1–O^1 bond fission, and the second (0.183 eV) appears at the instant of HCl formation in the transition point of this reaction, when $R(H^1–Cl^3)$ is 1.6 Å.

Thus, the reaction of thionyl chloride with a fluorinated alcohol in the presence of acid amides, yielding polyfluoroalkyl chlorosulfites, occurs as nucleophilic substitution, and the amide catalyst effects polarization of the starting reagents and transient structures.

1,1,5-Trihydroperfluoropentyl chlorosulfite. A mixture of 16.7 g of a fluorinated alcohol (n = 2) and 0.033 ml of *N*,*N*-dimethylacetamide (**VI**) was added, maintaining the temperature at –10°C, to 17.1 g of thionyl chloride. The reaction mixture was heated at 30°C for 3 h to remove hydrogen chloride. Excess $SOCl_2$ was removed by distillation, and the reaction product was distilled in a vacuum. Yield 19.33 g (85%), bp 64°C (5 mm Hg), d_4^{20} 1.7830, n_D^{20} 1.3630.

The other polyfluoroalkyl chlorosulfites were prepared in a similar way.

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