

UNSATURATED POLYFLUOROALKYL THIOCARBAMATES AND ISOTHIOCYANIDES BASED ON VINYLOXYETHYL ISOTHIOCYANIDE

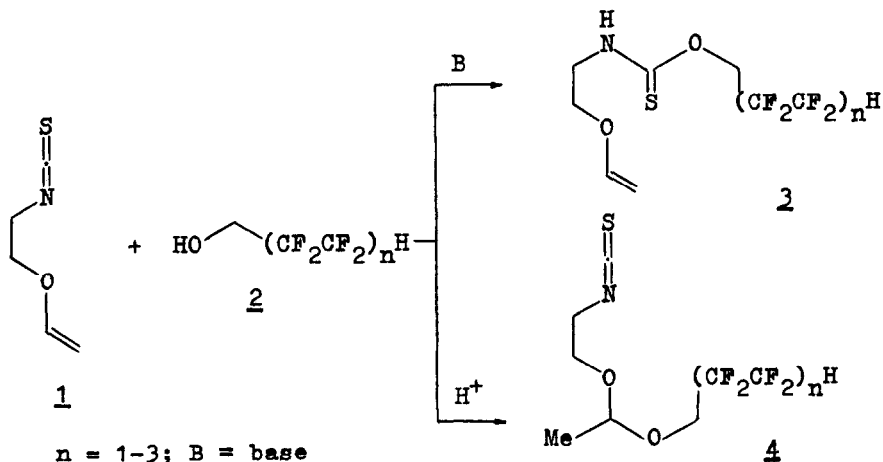
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Functionalized vinyl ethers are known to be valuable monomers and intermediates for organic synthesis.¹

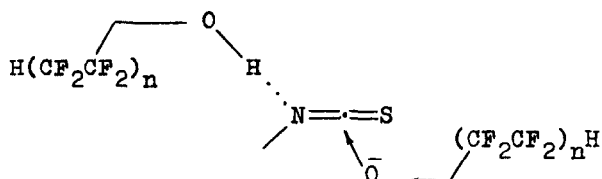
2-Vinyloxyethyl isothiocyanide (1) easily prepared from available 2-aminoethylvinyl ether² allows new types of functionalized polyfluoroorganic compounds, including new vinyloxy derivatives, to be produced.

The addition of polyfluoroalkanols (2) to 1 has been studied and the first representatives of to date unknown vinyl ethers of N-(2-hydroxyethyl)-O-polyfluoroalkyl thiocarbamic acid (3) as well as polyfluoroacetals containing an isothiocyanate group (4) have been prepared.



Unlike aliphatic alcohols, the addition of which to 1 even in the presence of strong bases is sluggish and ambiguous, polyfluoroalkanols 2 react readily with 1 to afford esters 3 in high yield

(up to 95%). This implies a concerted process in which the polyfluoroalkoxy anion attack onto the C=N bond is accompanied by simultaneous proton transfer from the second molecule of 2.



A considerable yield increase and milder reaction conditions in the case of $n = 3$ as compared with that of $n = 1$ are consistent with this scheme. Under electrophilic conditions alcohols 2 add smoothly to the vinyloxy group of 1 to give the corresponding acetals 4. Both processes are selective.

- 1 B.A. Trofimov, Heteroatomic Derivatives of Acetylene. New Polyfunctional Monomers, Reagents and Semiproducts, Nauka, Moscow, 1981, 319 p.
- 2 N.A. Nedolya, V.V. Gerasimova, B.A. Trofimov, Zh.Org.Khim., 21, No 9, p. 2019 (1985).