PERFLUOROALKYL-CHALCOGENATION OF OLEFINS

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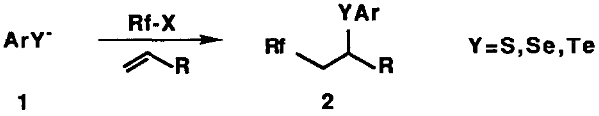
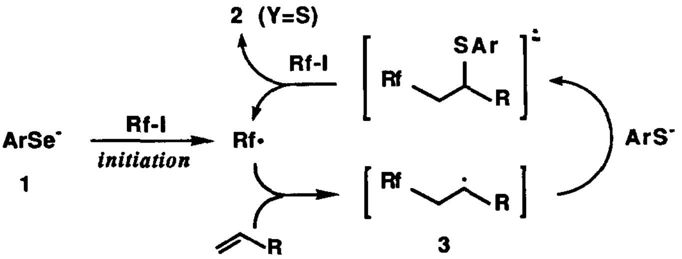
Perfluoroalkyl-chalcogenation of olefins has been performed by the reaction of chalcogenide anions with perfluoroalkylhalides (Rf-X) in the presence of olefins. Chalcogenide anion cleaves reductively the carbon-halogen bond of Rf-X, generating perfluoroalkyl radicals which undergo addition to C=C bond. The intermediate perfluoroalkylated radicals(3) react with ArY$^-$ via $S_{RN}1$ mechanism, propagating a chain reaction. The reactivity of the chalcogenide anion increases in the order of ArS$^-$ <ArSe$^-$<ArTe$^-$. Thus, telluride anion initiates the reaction even at -40°C. Because of the higher reactivity of selenide than thiolate, the selenide smoothly catalyzes perfluoroalkyl-sulfenylation. The catalytic cycle is shown in the following scheme.





[1] K.Uneyama and K.Kitagawa, *Tetrahedron Lett.*, **32**, 375 (1991)