CHLOROALKYLATION OF PENTAFLUOROTHIOPHENOL IN THE PRESENCE OF $AlCl_3$

T. D. Petrova, V. E. Platonov,
A. M. Maksimov, and I. S. Popova

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We have discovered a method for the polychloroalkylation of pentafluorophenol using CCl_4 as both reagent and solvent in the presence of $AlCl_3$ and showed that the primary trichloromethylation product, namely, pentafluorophenoxytrichloromethane is predominantly formed upon high dilution of the reaction mixture, while the major reaction product under other conditions is di(pentafluorophenyl) carbonate, which is obtained as a result of the hydrolysis of unstable di(pentafluorophenoxy)dichloromethane [1]. In the present work, we found that pentafluorothiophenol also undergoes polychloroalkylation upon the action of $CCl_4/AlCl_3$ but, in contrast to the reaction with pentafluorophenol, di(pentafluorophenylthio)dichloromethane is formed predominantly even under high dilution conditions; this dichloromethane is resistant to hydrolysis. The chloroalkylation of pentafluorothiophenol is rather general and also proceeds with $ArCX_3/AlCl_3$ (X = Cl, F with $CHCl_3$ as the solvent), leading to di(pentafluorophenylthio)arylchloromethanes.

$$C_6F_5SH \xrightarrow[2.\ H_2O]{1.\ RCX_3,\ AlCl_3} (C_6F_5S)_2CClR$$

$$X = R = Cl;\ X = Cl,\ R = C_6F_5,\ C_6H_5;\ X = F,\ R = C_6F_5,\ C_6H_5.$$

A sample of 0.006–0.01 mole pentafluorothiophenol with RCX_3 and $AlCl_3$ (in 1:1:3 mole ratio) was heated at 60–70°C over 6 h in 80 ml CCl_4 or $CHCl_3$. The reaction mixture was poured into cold water, extracted with ether, dried over $CaCl_2$. The solvents were distilled off. The solid residue was recrystallized from hexane and CCl_4 or sublimed. The product yield was 60%. The structures of these products were supported by elemental analysis, molecular mass determination, and IR and NMR spectroscopy.

LITERATURE CITED

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