THE POLYFLUOROPHENYLATION OF HALOSILANES, HALOGERMANES, AND HALOSTANNANES

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Perhaloalkanes react with trimethylchlorosilanes in the presence of $P(NEt_2)_3$ to form the corresponding perhaloalkyltrimethylsilanes and phosphonium salts [1-3]. Such transformations have not been described for aromatic compounds. We have found that the reaction of bromopolyfluorobenzenes with $P(NEt_2)_3$ and trialkylsilyl, trialkylgermyl, and trialkylstannyl halides is a convenient method for the preparation of polyfluorophenylsilanes, polyfluorophenylgermanes, and polyfluorophenylstannanes.

$$4\text{-}R'C_6F_4Br + P(NEt_2)_3 + R_3MX \xrightarrow[20°,1h]{} 4\text{-}R'C_6F_4MR_3 + (NEt_2)_3\ PXBr$$

R = Me, Et; R' = F, PrO, CF_3, M = Si, Ge, Sn; X = Cl, Br.

Chloropentafluorobenzene, bromobenzene, 3-bromotrifluoromethylbenzene, and benzyl chloride do not undergo this reaction under these conditions.

A solution of 50-54 mmoles $P(NEt_2)_3$ in 30 ml anhydrous ether or pentane was added dropwise with stirring in an argon stream to a solution of 50 mmoles C_6F_5Br and 55 mmoles R_3MX in 100 ml pentane, stirred for 1 h at 20°C, and filtered. The solvent was distilled off on a vacuum evaporator. The residue was filtered off and distilled in vacuum to give $C_6F_5SiMe_3$ in 66% yield, $C_6F_5GeEt_3$ in 57% yield, and $C_6F_5SnMe_3$ in 50% yield.

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