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SYNTHESIS OF SUBSTITUTED BENZYLTRIMETHYLSILANES

FROM TETRAMETHYLAMONIUM TETRAKIS(TRIMETHYLSILYLMETHYL)

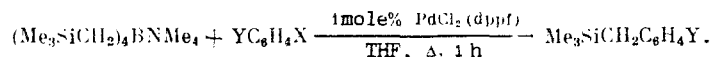
BORATE AND ARYL HALIDES

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Substituted benzyltrimethylsilanes are obtained in the reaction of the corresponding benzylmagnesium halides with trimethylchlorosilane [1]. When the benzyl halide molecule has substituents sensitive to the active organometallic compounds, the reaction of benzyl halides with hexamethyldisilane catalyzed by palladium complexes may be used for synthesis [2]. However, the reaction is carried out under very vigorous conditions (120-180°C for 10-90 h) and the yield of $\text{ArCH}_2\text{SiMe}_3$ in a number of cases does not exceed 6-8%.

We have shown that tetramethylammonium tetrakis(trimethylsilylmethyl) borate reacts with aryl halides in THF at reflux in the presence of $\text{PdCl}_2(\text{dppf})$ [dppf = 1,1'-bis(diphenylphosphino)ferrocene] with the formation of the corresponding benzyltrimethylsilanes in high yields.



When Y = p-Cl and X = I in $\text{YC}_6\text{H}_4\text{X}$, the yield of the cross-coupling product was 72%. When Y = p-Cl and X = Br, the yield of the cross-coupling product was 98%. When Y = p-Ac and X = Br, the yield of the cross-coupling product was 75%. When Y = m-NO₂ and X = I, the yield of the cross-coupling product was 72%. The yields were determined by gas-liquid chromatography.

Under the given conditions, $(\text{Me}_3\text{SiCH}_2)_4\text{BLi}$ proved less reactive. The yield in the reaction with p-ClC₆H₄I after 80 min was 19%. The addition of water to the reaction mixture ($\text{H}_2\text{O}:\text{THF} = 1:4$) leads to an acceleration of the reaction. The yield of p-ClC₆H₄CH₂SiMe₃ after 2 h was 83%.

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