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CATALYSIS OF THE REACTION OF GRIGNARD REAGENTS WITH SILICON, TIN, PHOSPHORUS, AND ARSENIC HALIDES AND ORGANOHALIDES BY COPPER SALTS WITH THE FORMATION OF ORGANIC COMPOUNDS OF THESE ELEMENTS

L. I. Zakharkin and E. V. Anikina

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The catalysis of the cross coupling of Grignard reagents with alkyl halides by copper salts and their complexes is commonly used in organic synthesis for the formation of new C-C bonds. In the present work, we have found that CuI, CuBr, and Li_2CuCl_4 catalyze the reaction of Grignard reagents with Si, Sn, P, and As halides and organohalides with the formation of organic compounds of these elements.

The formation of tetraarylsilanes upon the reaction of arylmagnesium halides with $SiCl_4$ proceeds only above 160°C [1]. The reaction of $SiCl_4$ and $PhSiCl_3$ with C_6H_5MgCl and $p\text{-}CH_3C_6H_4MgCl$ in THF in the presence of catalytic amounts of CuI or Li_2CuCl_4 at −5°C and heating of the solution at reflux gives Ph_4Si [1] and $(p\text{-}CH_3C_6H_4)_4Si$ [2] with yields above 70%.

$$ArMgCl + SiCl_4 \xrightarrow[CuI \text{ or } Li_2CuCl_4]{THF} Ar_4Si$$

$$PhSiCl_3 + PhMgCl \xrightarrow[Li_2CuCl_4]{THF} Ph_4Si$$

$$Ar = Ph,\ p\text{-}CH_3C_6H_4.$$

The reaction of $PhSiCl_3$ with PhMgCl in THF solution without catalyst does not give Ph_4Si but rather Ph_3SiCl. The reaction of PhMgCl with $SnCl_4$ in THF solution proceeds more completely in the presence of Li_2CuCl_4 with the formation of Ph_4Sn. The yield does not exceed 80%. Analogously, the reaction of PhMgCl and $p\text{-}CH_3C_6H_4MgCl$ with PCl_3 and $AsCl_3$ in THF solution in the presence of CuI and Li_2CuCl_4 proceeds readily.

$$ArMgCl + ECl_3 \xrightarrow[Li_2CuCl_4]{THF} Ar_3E$$

$$E = P, As;\ Ar = Ph,\ p\text{-}CHC_6H_4.$$

The use of copper catalysts in this reaction also leads to purer products.

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