Manganese-Catalyzed Cross-Coupling of Aryl Halides and Grignard Reagents by a Radical Mechanism

The substrate scope and the mechanism have been investigated for the MnCl₂-catalyzed cross-coupling reaction between aryl halides and Grignard reagents. The transformation proceeds rapidly and in good yield when the aryl halide component is an aryl chloride containing a cyano or an ester group in the para position or a cyano group in the ortho position. A range of other substituents gave no conversion of the aryl halide or led to the formation of side products. A broader scope was observed for the Grignard reagents, where a variety of alkyl- and arylmagnesium chlorides participated in the coupling. Two radical-clock experiments were carried out, and in both cases an intermediate aryl radical was successfully trapped. The cross-coupling reaction is therefore believed to proceed by an SR₄N₁ mechanism, with a triorganomanganate complex serving as the most likely nucleophile and single-electron donor. Other mechanistic scenarios were excluded based on the substrate scope of the aryl halide.

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