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Cobalt-catalyzed Trimethylsilylmethylmagnesium-Promoted Radical Alkenylation of Alkyl Halides: A Complement to the Heck Reaction

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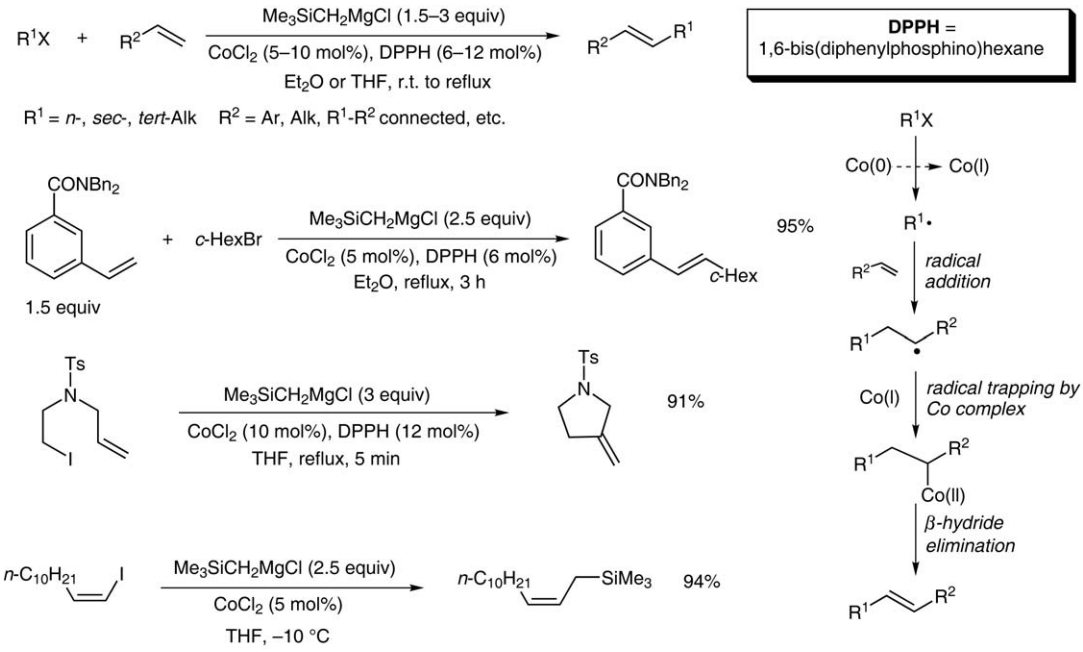
Co-Catalyzed Radical Alkenylation of Alkyl Halides



Significance: This work describes a novel method of intermolecular coupling of alkenes with alkyl halides in the presence of trimethylsilylmethylmagnesium chloride and a cobalt catalyst $CoCl_2$-1,6-bis(diphenylphosphino)hexane. In many cases it is an alternative to the Heck reaction because it does not require expensive palladium catalysts. This method shows good functional-group compatibility. The reaction proceeds via a radical pathway. An intramolecular version of this process allows to create complex carbon frameworks. Additionally, a Co-catalyzed cross-coupling of iodoalkenes with Me_3SiCH_2MgCl leading to allyltrimethylsilanes is described.

Comment: This original method is especially convenient for the synthesis of polysubstituted styrenes, including those bearing functional groups. Mechanistically, the key steps of the process are the formation of a radical from the alkyl halide, its addition to the double bond and the trapping of the product by the Co(I) complex. Since the process is of radical nature, either a styrene has to be used to ensure the selective radical attack, or the reaction has to be performed intramolecularly, affording cyclization products. Interestingly, trimethylsilylmethyl magnesium halide is a unique Grignard reagent, allowing to perform such transformations. The reaction has obviously a high synthetic potential.

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