W. AFFO, H. OHMIYA, T. FUJIOKA, Y. IKEDA, T. NAKAMURA, H. YORIMITSU,* K. OSHIMA,* Y. IMAMURA, T. MIZUTA, K. MIYOSHI (KYOTO UNIVERSITY AND HIROSHIMA UNIVERSITY, JAPAN)

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

J. Am. Chem. Soc. 2006, 128, 8068-8077.

Co-Catalyzed Radical Alkenylation of Alkyl **Halides**

$$R^{1}X + R^{2} \xrightarrow{\text{CoCl}_{2} (5-10 \text{ mol}\%), \text{DPPH } (6-12 \text{ mol}\%)} Et_{2}O \text{ or THF, r.t. to reflux}$$

$$R^{1} = n\text{-}, \text{ sec., tert-Alk} \quad R^{2} = \text{Ar, Alk, R}^{1} \cdot R^{2} \text{ connected, etc.}$$

$$R^{1}X + CONBn_{2} \xrightarrow{\text{CoNBn}_{2}} \text{CoCl}_{2} (5 \text{ mol}\%), \text{DPPH } (6 \text{ mol}\%)$$

$$Et_{2}O \text{ reflux}$$

$$CONBn_{2} \xrightarrow{\text{CoNBn}_{2}} \text{CoOl}_{2} (5 \text{ mol}\%), \text{DPPH } (6 \text{ mol}\%)$$

$$Et_{2}O, \text{ reflux, 3 h}$$

$$R^{2} \xrightarrow{\text{radical addition}} \text{R}^{2}$$

$$R^{2} \xrightarrow{\text{radical trapping by Co complex}} \text{CoOl}_{2} (10 \text{ mol}\%), \text{DPPH } (12 \text{ mol}\%)$$

$$THF, \text{ reflux, 5 min}$$

$$R^{2} \xrightarrow{\text{CoOl}_{2} (5 \text{ mol}\%)} \text{CoCl}_{2} (5 \text{ mol}\%)$$

$$THF, -10 ^{\circ}C$$

$$R^{1} \xrightarrow{\text{Re}^{2}} \text{CoOl}_{1} \xrightarrow{\text{Re}^{2}} \text{CoOl}_{2} (10 \text{ mol}\%)$$

$$R^{1} \xrightarrow{\text{Re}^{2}} \text{CoOl}_{1} \xrightarrow{\text{Re}^{2}} \text{CoOl}_{2} (10 \text{ mol}\%)$$

$$R^{1} \xrightarrow{\text{Re}^{2}} \text{CoOl}_{2} (10 \text{ mol}\%)$$

$$R^{2} \xrightarrow{\text{Re}^{2}} \text{Re}^{2}$$

$$R^{2} \xrightarrow{\text{Re}^{2}} \text{Re}^$$

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 CoCl₂-1,6bis(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 Me₃SiCH₂MgCl 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.

Synfacts 2006, 8, 0825-0825 Published online: 21.07.2006 Category

Metal-Mediated Synthesis

Key words

Heck reaction cobalt catalysis radical addition

SYNFACTS Contributors: Paul Knochel, Andrei Gavryushin DOI: 10.1055/s-2006-941997; Reg-No.: P06706SF