Highly Stereo- and Chemoselective Iron-Catalyzed Alkenylation of Organomagnesium Compounds


Iron-Catalyzed Alkenylation of Organomagnesium Reagents

\[
\begin{align*}
R^1 & \quad \text{R}^2 \quad \text{X} & \quad \text{Fe(acac)}_3 & \quad (1 \text{ mol\%}) \\
(1.0 \text{ equiv}) & \quad \text{(1.1 equiv)} & \quad \text{NMP} & \quad (9.0 \text{ equiv}), \text{THF} \\
\end{align*}
\]

\[
\begin{align*}
\text{R}^1, \text{R}^2, \text{R}^3 & = \text{H}, \text{Alk}, \text{Ar} \\
\text{X} & = \text{Cl, Br, I} \\
\end{align*}
\]

Selected examples:

- \( \text{Hex} \text{n-Bu} \) 75% yield, \( E/Z > 99:1 \)
- \( \text{Hex} \text{n-Bu} \) 80% yield, \( Z/E > 99:1 \)
- \( \text{Ph} \text{i-Pr} \) 73% yield
- \( \text{n-Bu} \) 89% yield
- \( \text{n-Bu} \) 82% yield
- \( \text{CaH}_{17} \) 86% yield
- \( \text{CaH}_{17} \) 84% yield
- \( \text{n-Bu} \) 75% yield
- \( \text{AcO} \text{i-Pr} \) 72% yield
- \( \text{O} \text{n-Bu} \) 80% yield
- \( \text{O} \text{n-Bu} \) 68% yield
- \( \text{O} \text{n-Bu} \) 79% yield
- \( \text{Cl} \text{n-Bu} \) 79% yield

**Significance:** In 1998, Cahiez and Avedissian reported a general method for the iron-catalyzed cross-coupling between alkenyl halides (halide = Cl, Br, or I) and Grignard reagents in high yields and excellent diastereoselectivities (>99:1).

**Comment:** The approach significantly improved the cross-coupling between alkenyl halides and Grignard reagents using Fe(acac)_3 as catalyst. Additionally, it was found that the use of a polar co-solvent such as NMP was crucial for the cross-coupling to proceed in excellent yields. Furthermore, functional groups such as ketones were tolerated for the first time in these cross-coupling reactions (see Review below).