Heterogeneous One-Pot Carbonylation and Mizoroki–Heck Reaction in a Parallel Manner Following the Cleavage of Cinnamaldehyde Derivatives


Parallel Carbonylation and Decarbonylative Heck Reaction on Palladium/Carbon

**Significance:** Palladium on carbon (Pd/C) catalyzed the carbonylation of aryl iodides with terephthalaldehyde as a CO source to give the corresponding products in up to 98% yield (eq. 1; 17 examples). A simultaneous parallel decarbonylative Mizoroki–Heck reaction of cinnamaldehydes with iodobenzenes (tube A) and carbonylation of 2-iodobenzyl alcohol or 2-iodobenzamide with the CO generated in situ (tube B) were carried out in the presence of Pd/C in an H-shaped tube to give trans-stilbenes and a phthalide or phthalimide, respectively (eq. 2; 6 examples).

**Comment:** No recyclability of Pd/C was observed in the parallel decarbonylative Mizoroki–Heck reaction of 4-methoxycinnamaldehyde with iodobenzene and carbonylation of 2-iodobenzyl alcohol (first reuse: 4-methoxy-trans-stilbene: 0% yield; phthalide: trace).

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**Equation 1:**

\[
\text{Ar} \rightarrow \underbrace{\text{CHO}}_{(1 \text{ equiv})} + \text{Ph}_3\text{P} (40 \text{ mol\%}) + \text{NMP}, \text{N}_2, 100 \degree \text{C}, 24 \text{ h} \rightarrow \text{Ar} \rightarrow \underbrace{\text{OR}}_{(1 \text{ equiv})} \text{R}^1 \text{R}^2 \text{N}^m \text{H} + \text{R}^3 \text{R}^4 \text{N}^m \text{H} \text{Ph} + \text{R}^5 \text{N}^m \text{H} \text{Ph} \text{ (up to 98\% yield)}
\]

**Selected results:**

- \( \text{R}^2 = \text{H}, 88\% \text{ yield} \)
- \( \text{R}^2 = \text{Ac}, 85\% \text{ yield} \)
- \( \text{R}^2 = \text{NO}_2, 87\% \text{ yield} \)
- \( \text{R}^2 = \text{OMe}, 75\% \text{ yield} \)

**Equation 2:**

\[
\begin{align*}
\text{R}^2 = \text{H}, & & \text{85\% yield} \\
& & \text{(from 2-HOCH}_2\text{C}_6\text{H}_4\text{I in i-PrOH)}
\end{align*}
\]

**Selected results:**

- \( \text{R}^2 = \text{H}, 85\% \text{ yield} \)
- \( \text{R}^1 = \text{Et}, 59\% \text{ yield} \)
- \( \text{R}^1 = \text{n-Pr}, 59\% \text{ yield} \)
- \( \text{R}^1 = \text{n-Pent}, 64\% \text{ yield} \)
- \( \text{R}^1 = \text{Me}, 54\% \text{ yield} \)

- \( \text{R}^3 = \text{H}, 85\% \text{ yield} \)
- \( \text{R}^3 = \text{Me}, 98\% \text{ yield} \)
- \( \text{R}^3 = \text{Me}, 85\% \text{ yield} \)
- \( \text{R}^3 = \text{Me}, 95\% \text{ yield} \)

- \( \text{R}^1 = \text{H}, 88\% \text{ yield} \)
- \( \text{R}^1 = \text{Ac}, 85\% \text{ yield} \)
- \( \text{R}^1 = \text{NO}_2, 87\% \text{ yield} \)
- \( \text{R}^1 = \text{OMe}, 75\% \text{ yield} \)