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A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation

Hydrogenolysis of Aryl or Benzyl Ethers Using Nickel Nanoparticles

**Hydrogenolysis of aryl ethers:**

\[
\begin{align*}
\text{Ni(CH}_2\text{TMS)}_2(\text{TMEDA}) \\
(0.25–10 \text{ mol%}) \\
\text{NaO-Bu (2.5 equiv)} \\
\text{H}_2 (1 \text{ atm}), m\text{-xylene} \\
120 ^\circ C, 41–96 \text{ h}
\end{align*}
\]

Selected substrates:

- 2a 99% yield, 3a 99% yield
- 2b 99% yield, 3b 99% yield
- 2c 68% yield, 3c 66% yield
- 2d 94% yield, 3d 91% yield
- 2e 13% yield, 3e 11% yield
- 4e 81% yield, 5e 85% yield
- 2f 3% yield, 3f 3% yield
- 4f 90% yield, 5f 90% yield
- 2g–3g 160% yield (based on 1)
- 5g 9% yield

Selected results:

- 2a 99% yield, 3a 99% yield
- 2b 99% yield, 3b 99% yield
- 2c 68% yield, 3c 66% yield
- 2d 94% yield, 3d 91% yield
- 2e 13% yield, 3e 11% yield
- 4e 81% yield, 5e 85% yield
- 2f 3% yield, 3f 3% yield
- 4f 90% yield, 5f 90% yield
- 2g–3g 160% yield (based on 1)
- 5g 9% yield

**Hydrogenolysis of benzyl ethers:**

\[
\begin{align*}
\text{Ni(CH}_2\text{TMS)}_2(\text{TMEDA}) \\
(0.25–10 \text{ mol%}) \\
\text{NaO-Bu (2.5 equiv)} \\
\text{H}_2 (1 \text{ atm}), m\text{-xylene} \\
120 ^\circ C, 48–96 \text{ h}
\end{align*}
\]

Selected results:

- 7a 98% yield, 8a 95% yield
- 7b 81% yield, 8b 87% yield
- 7c 93% yield, 8c 98% yield

**Significance:** Nickel nanoparticles, generated in situ from \(\text{Ni(CH}_2\text{TMS)}_2(\text{TMEDA})\) and \(\text{t-BuONa}\), catalyzed the hydrogenolysis of aryl ethers 1 under \(\text{H}_2\) in \(m\text{-xylene}\) to give the corresponding products 2–5 (15 examples). The hydrogenolysis of benzyl ethers 6 also proceeded in the presence of the nickel nanoparticles under \(\text{H}_2\) atmosphere to afford the corresponding toluenes 7 and phenols 8 (4 examples).

**Comment:** The nickel nanoparticles were characterized by TEM, STEM, and EDS analyses. EDS analysis showed that the catalyst contained both nickel and sodium. From this result, the authors propose that \(\text{t-BuONa}\) stabilizes the nickel nanoparticles.