Hydrogenolysis of Aryl or Benzyl Ethers Using Nickel Nanoparticles

**Significance:** Nickel nanoparticles, generated in situ from Ni(CH₂TMS)₂(TMEDA) and t-BuONa, catalyzed the hydrogenolysis of aryl ethers 1 under H₂ in m-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 H₂ 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 t-BuONa stabilizes the nickel nanoparticles.

**Hydrogenolysis of aryl ethers:**

\[ \text{Ni(CH}_2\text{TMS)}_2\text{(TMEDA)} \quad \text{NaOH-Bu (2.5 equiv)} \]

\[ \text{H}_2 (1 \text{ atm}) \quad \text{m-xylene} \quad 120 \degree \text{C, } 41-96 \text{ h} \]

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

Hydrogenolysis of benzyl ethers:

\[ \text{Ni(CH}_2\text{TMS)}_2\text{(TMEDA)} \quad \text{NaOH-Bu (2.5 equiv)} \]

\[ \text{H}_2 (1 \text{ atm}) \quad \text{m-xylene} \quad 120 \degree \text{C, } 48-96 \text{ h} \]

Selected results:

7a 98% yield, 8a 95% yield

7b 81% yield, 8b 87% yield

7c 93% yield, 8c 98% yield