Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

Reduction of nitroarenes using the batch system:

\[
\begin{align*}
\text{R-NO}_2 & \quad \text{Fe(acac)}_3 (0.25 \text{ mol%}) \\
& \quad \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} (1.2 \text{ equiv}) \\
& \quad \text{MeOH} \\
& \quad \text{MW, 150 °C, 2–8 min} \\
\rightarrow & \quad \text{R-NH}_2
\end{align*}
\]

(eq. 1)

Selected examples:

- 2 min, 99% yield
- 2 min, 99% yield
- 8 min, 99% yield
- 4 min, 99% yield
- 6 min, 99% yield
- 6 min, 95% yield
- 4 min, 99% yield
- 2 min, 99% yield
- 4 min, 98% yield

Continuous-flow reduction of nitroarenes:

\[
\begin{align*}
\text{ca. 1.0 M solution in MeOH} & \quad \text{Fe(acac)}_3 (0.25 \text{ mol%}) \\
& \quad \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} (1.2 \text{ equiv}) \\
& \quad \text{MeOH, 150–170 °C} \\
& \quad 6–12 \text{ mL/min} \\
& \quad \text{residence time: 1.3–1.6 min} \\
\rightarrow & \quad \text{R-NH}_2
\end{align*}
\]

(eq. 2)

Significance: Iron oxide nanocrystals, generated in situ from Fe(acac)_3 and hydrazine hydrate, catalyzed the reduction of nitroarenes with hydrazine hydrate under microwave conditions to give the corresponding anilines in 95–99% yield (20 examples, eq. 1). In the reduction of nitrobenzene to aniline using the batch system, the catalyst was magnetically separated from the reaction mixture and reused seven times.

Comment: The reduction of nitroarenes was also performed using a continuous-flow system to afford the anilines in 95–97% yield (eq. 2). The in situ generated iron oxide nanoparticles were characterized by XRD and HRTEM analyses. ICP–MS showed 7.9% iron leaching from the catalyst during the reduction using the batch system.