CHM 422 Organic Synthesis, Dr. Laurie S. Starkey Common Reduction Reactions

NHR'

catalytic* hydrogenation

$$R \xrightarrow{\qquad} R \xrightarrow{H_2, \text{ cat.}} R - CH_2 CH_2 \cdot R$$

*catalyst = Pd, Pt, Ni or
Ru or Rh organometallic reagents
such as RhCl[PPh₃]₃

$$R-C\equiv N \xrightarrow{H_2, \text{ cat.}} R-CH_2NH_2$$

$$\begin{array}{ccc} R-NO_2 & \xrightarrow{H_2, \text{ cat.}} & R-NH_2 \\ \hline \end{array}$$

useful reactions for the synthesis of amines

$$-CH_2OR \xrightarrow{H_2, cat.} -CH_3 + ROH$$

Since the benzylic position is easily reduced, the benzyl group (PhCH₂–) is commonly used to protect alcohols.

hydride reagents

$$\begin{array}{c|ccccc}
O & & LiAlH_4 \ or & & H & OH \\
R & & & NaBH_4 & & R & R
\end{array}$$

$$\begin{array}{c|ccccc}
O & & LiAlH_4 & & H & H \\
OR' & & & only & & R'=alkyl \ (ester) & & & \\
O & & & LiAlH_4 & & H & H
\end{array}$$

Note: Lithium aluminum hydride (LAH) reductions are always followed by an aqueous workup (H_3O^+). NaBH₄ is less reactive and can be used with protic solvents (ROH).

DIBAL-H, diisobutylaluminum hydride, reduces esters and nitriles to aldehydes

metal reagents

$$R \xrightarrow{\qquad} R \xrightarrow{\qquad Na \text{ or Li} \qquad H \qquad R}$$

$$NH_3 \qquad R \qquad H$$

Dissolving metal reduction gives *trans* alkene product.

$$CH_3$$
 \longrightarrow NH_3 CH_3

Birch reduction gives 1,4-diene products.

$$\begin{array}{ccc}
O & & Zn/Hg & H & H \\
R & & & HCI & R
\end{array}$$

Clemmensen or Wolff-Kishner (NH₂NH₂, KOH) reduction converts a carbonyl to a methylene. Conversion can also be done by reduction of the dithiane (HSCH₂CH₂CH₂SH; Raney Ni).