1. Recall as pka increases, strength of X-H bond increases or acidity decreases.

\[
\begin{array}{c}
\overset{\circ}{\text{O}} \\
\text{OH}
\end{array}
\]  

The acid is most acidic: 4.76

\[
\begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\]

Pyridinium is next most acidic: 5.21

Any electronic induction destabilizes the nitration. Sometimes used as a weak acid.

\[
\begin{array}{c}
\overset{\text{+}}{\text{H}} \\
\text{N}
\end{array}
\]

Imidazolium is next, not as much aromatic character as pyridinium so not as much nitration destabilization. Note: protonation of the first nitrogen would destroy aromaticity.

2. \(\text{NH}_2\)

Lone pair on free base is fairly stable with a proton destroys localized negative charge.

\[
\begin{array}{c}
\overset{\circ}{\text{O}} \\
\text{NH}
\end{array}
\leftrightarrow
\begin{array}{c}
\overset{\circ}{\text{O}} \\
\text{NH}
\end{array}
\]

Amides aren't as acidic as ammonium ions, comparable to alcohols due to very little contribution from nitramion.

\[
\begin{array}{c}
\overset{\text{O}}{\text{N}} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\overset{\circ}{\text{O}} \\
\text{NH}
\end{array}
\]

Neutral amines aren't acidic at all - they're bases.
2. \[
\begin{align*}
\text{NH}_2 \quad \text{MeI} \quad \text{NaN}\text{t} & \quad \text{NH}_2 \\
\text{NH} & \quad \text{NH} \\
\text{N} & \quad \text{N} \\
\text{+} & \quad \text{+} \\
\text{Me}^+ & \quad \text{+} \quad \text{N}_3^- \\
\end{align*}
\]

*Note:* MeI + NaH $\rightarrow$ No Reaction because hydride is not nucleophilic, just basic.

3. pg 880

\[
\begin{align*}
\text{NH}_2 & \quad \text{Ce}^{4+}, \\
\text{pyridine} & \quad \text{H}^+ \text{A} \\
\text{NH} & \quad \text{NH} \\
\end{align*}
\]

Multiple addition doesn't occur because amides are poor nucleophiles. Other reductions are possible.

4. pg 876

\[
\begin{align*}
\text{NH}_2 & \quad \text{H}^+ \quad \text{H}^+ \text{A} \\
\text{with} & \quad \text{H}_2\text{O} \\
\text{NH} & \quad \text{NH} \\
\text{purify amine} & \quad \text{isolated} \\
\end{align*}
\]

Ammonium ions are difficult to purify, and react with $\text{H}_2\text{O}$ after reduction to overalkylate. So use ONLY catalytic amounts of acid.

Again, other reductions besides LiAlH$_4$ are possible.
Many other pathways are possible.

Modified Gabriel synthesis, because deprotonated amide is a good nucleophile and neutral amide is not. Other pathways possible.

For example:

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