\( \alpha \)-Arylation of Ketones

**Significance:** The palladium-catalyzed \( \alpha \)-arylation of ketones was reported simultaneously and independently by Buchwald and Hartwig (J. Am. Chem. Soc. 1997, 119, 12382). The use of BINAP or Tol-BINAP was necessary for this transformation, while Hartwig employed ferrocene-based bisphosphines. Prior to these reports, \( \alpha \)-arylation required silyl enol ethers and lead and bismuth compounds.

**Comment:** The products were obtained in good to high yields. Excellent ratios of monoarylated to diarylated products were obtained, as well as high regioselectivity and functional group tolerance. The mechanism is proposed to occur through oxidative addition of palladium(0) with the aryl bromide, ligand substitution by the sodium enolate, and reductive elimination.

**Selected examples:**

- **76% yield**
  
  \[
  \begin{align*}
  \text{O} & \text{O} \\
  \text{O} & \text{O} \\
  \text{Ph} & \text{Ph}
  \end{align*}
  \]

- **91% yield**
  
  \[
  \begin{align*}
  \text{Ph} & \text{Ph} \\
  \text{Ph} & \text{Ph}
  \end{align*}
  \]

- **63% yield**
  
  \[
  \begin{align*}
  \text{O} & \text{O} \\
  \text{Ph} & \text{Ph}
  \end{align*}
  \]

- **83% yield**
  
  \[
  \begin{align*}
  \text{O} & \text{O} \\
  \text{t-Bu} & \text{t-Bu}
  \end{align*}
  \]

- **75% yield**
  
  \[
  \begin{align*}
  \text{Ph} & \text{Ph} \\
  \text{t-Bu} & \text{t-Bu}
  \end{align*}
  \]

- **93% yield**
  
  \[
  \begin{align*}
  \text{O} & \text{O} \\
  \text{t-Bu} & \text{t-Bu}
  \end{align*}
  \]

**Proposed mechanism:**

The mechanism is proposed to occur through oxidative addition of palladium(0) with the aryl bromide, ligand substitution by the sodium enolate, and reductive elimination.