Nickel-Catalyzed Bromide-to-Iodide Aromatic Finkelstein Reaction

**Significance:** In 1978, Takagi, Hayama, and Okamoto disclosed an early example of a halogene exchange reaction using a simple nickel(II) precatalyst, with added Zn or PbBu3, and a nucleophilic source of iodide (KI). As the authors explain, at this time the most common strategy to perform an aromatic Finkelstein reaction was to use copper; however, the ability to go from a bromide to iodide was unattainable. This topic has remained of interest for the last 50 years, with notable contributions from a wide variety of groups.

**Comment:** The addition of Zn was crucial for the reaction to occur at lower temperatures. Moreover, it was found that the addition of a donating phosphine ligand, such as PbBu3, suppressed the formation of the reductive homocoupled side product. At elevated temperatures, only the phosphine additive was necessary for a successful reaction, without the need of the Zn reductant. The reaction did not occur when using various nickel(0) precatalysts.

**Substrate scope:**

- **conditions A:** 77% yield + 15% HC
- **conditions A:** + PbBu3: 74% yield + 5% HC
- **conditions B:** 140 °C, 89% yield, no HC
- **conditions A:** 81% yield + 9% HC + <1% diiodobenzene
- **conditions B:** 153 °C, 42% yield

**From aryl chloride:**

- **conditions B, 150 °C**

13% yield