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Redox-Neutral Organometallic Elementary Steps at Bismuth: Catalytic Synthesis of Aryl Sulfonyl Fluorides

Chem. Lett. **1978**, 7, 191–192, DOI: 10.1246/cl.1978.191.

Nickel-Catalyzed Bromide-to-Iodide Aromatic Finkelstein Reaction

Substrate scope:

conditions A: 77% yield + 15% HC
conditions A: + PBU₃: 74% yield + 5% HC
conditions B: 140 °C, 89% yield, no HC

conditions A: 78% yield + 16% HC

conditions A: 76% yield + 22% HC

conditions A: 81% yield + 9% HC
+ <1% diiodobenzene

conditions B: 153 °C, 42% yield

From aryl chloride:

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 PBU₃, 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.

Review: D. A. Petrone, J. Ye, M. Lautens *Chem. Rev.* **2016**, 116, 8003–8104.

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 PBU₃, 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.

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