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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-lodide Aromatic Finkelstein Reaction

#### conditions A:

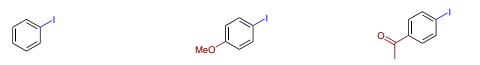
NiBr<sub>2</sub> (2–4 mol%, 0.17 M in DMF)
Zn<sup>0</sup> (17 mol%), KI (2.5 equiv), 50 °C
HMPA, N<sub>2</sub>, 1.5–3 h

conditions B:
NiBr<sub>2</sub> (2.5–4 mol%)

NiBr<sub>2</sub> (2.5–4 mol%) PBu<sub>3</sub> (5–8 mol%), KI (3.0 equiv) 140–153 °C, DMF, N<sub>2</sub>, 12–24 h

minor homocoupled side product (HC)

### Substrate scope:



conditions A: 77% yield + 15% HC conditions A: + PBu<sub>3</sub>: 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 PBu<sub>3</sub>, 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.

SYNFACTS Contributors: Mark Lautens, Austin D. Marchese Synfacts 2022, 18(03), 0293 Published online: 16.02.2022 **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 PBu<sub>3</sub>, 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.

## Category

**Metals in Synthesis** 

#### Key words

nickel catalysis aryl iodides halogen exchange

