Hypervalent Iodine for α,α-Dihalogenation

**Chlorination:**

Selected examples:

- PhICl₂ (1.1 equiv) pyridine (5 mol%) CH₂Cl₂
  - 87% yield
  - 67% yield
  - 89% yield

Fluorination:

Selected examples:

- TolIF₂ (1.1 equiv) BF₃·OEt₂ (1 mol%) PhCl, 110 °C 5 min
  - 95% yield
  - 79% yield
  - 89% yield

**Significance:** Functionalization at the α-position of carbonyls represents one of the most versatile and useful types of transformations in organic chemistry. In this paper, the authors describe the use of a hypervalent iodine species to doubly halogenate the α-position of esters with either chlorine or fluorine.

**Comment:** While the chlorination procedure was shown to be broadly functional group tolerant, the need for BF₃·OEt₂ in the case of fluorination limits the possible functionality in the starting material. The authors report that substrates with labile moieties such as OMe or NHAc decompose upon heating with BF₃·OEt₂.