Hypervalent Iodine for $\alpha,\alpha$-Dihalogenation

**Chlorination:**

\[
\text{PhCl}_2 \text{ (1.1 equiv)} \quad \text{pyridine (5 mol\%)} \quad \text{CH}_2\text{Cl}_2
\]

**Selected examples:**

- $\text{BrClCl}$: 87% yield
- $\text{O}_{2}\text{N} \text{ClCl}$: 67% yield
- $\text{TsO} \text{ClCl}$: 89% yield

- $\text{MeO} \text{ClCl}$: 95% yield
- $\text{O}_{2}\text{N} \text{ClCl}$: 79% yield
- $\text{TsO} \text{ClCl}$: 89% yield

**Fluorination:**

\[
\text{TolIF}_2 \text{ (1.1 equiv)} \quad \text{BF}_3 \cdot \text{OEt}_2 \text{ (1 mol\%)} \quad \text{PhCl, 110 °C} \quad 5 \text{ min}
\]

**Selected examples:**

- $\text{BrF}_2$: 66% yield
- $\text{O}_{2}\text{N} \text{F}_2$: 79% yield
- $\text{TsO} \text{F}_2$: 74% yield

- $\text{MeO} \text{F}_2$: 79% yield
- $\text{O}_{2}\text{N} \text{F}_2$: 26% yield
- $\text{TsO} \text{F}_2$: 17% yield

**Significance:** Functionalization at the $\alpha$-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 $\alpha$-position of esters with either chlorine or fluorine.

**Comment:** While the chlorination procedure was shown to be broadly functional group tolerant, the need for BF$_3$·OEt$_2$ 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 BF$_3$·OEt$_2$. 