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

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 $\text{BF}_3\cdot\text{OEt}_2$ 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 $\text{BF}_3\cdot\text{OEt}_2$. 

Selected examples:

**Chlorination:**

- $\text{Br} - \text{Cl} - \text{Cl}$ (87% yield)
- $\text{O}_2\text{N} - \text{Cl} - \text{Cl}$ (67% yield)
- $\text{TsO} - \text{Cl} - \text{Cl}$ (89% yield)
- $\text{OMe} - \text{Cl} - \text{Cl}$ (95% yield)
- $\text{MeO} - \text{Cl} - \text{Cl}$ (79% yield)
- $\text{OBn} - \text{Cl} - \text{Cl}$ (26% yield)

**Fluorination:**

- $\text{Br} - \text{F} - \text{F}$ (66% yield)
- $\text{O}_2\text{N} - \text{F} - \text{F}$ (79% yield)
- $\text{TsO} - \text{F} - \text{F}$ (74% yield)
- $\text{OMe} - \text{F} - \text{F}$ (79% yield)
- $\text{MeO} - \text{F} - \text{F}$ (26% yield)
- $\text{OBn} - \text{F} - \text{F}$ (17% yield)