Control of Regioselectivity in Hypervalent Iodine-mediated Sulfonyloxylactonization by Noncovalent Interactions in Ion Pairs

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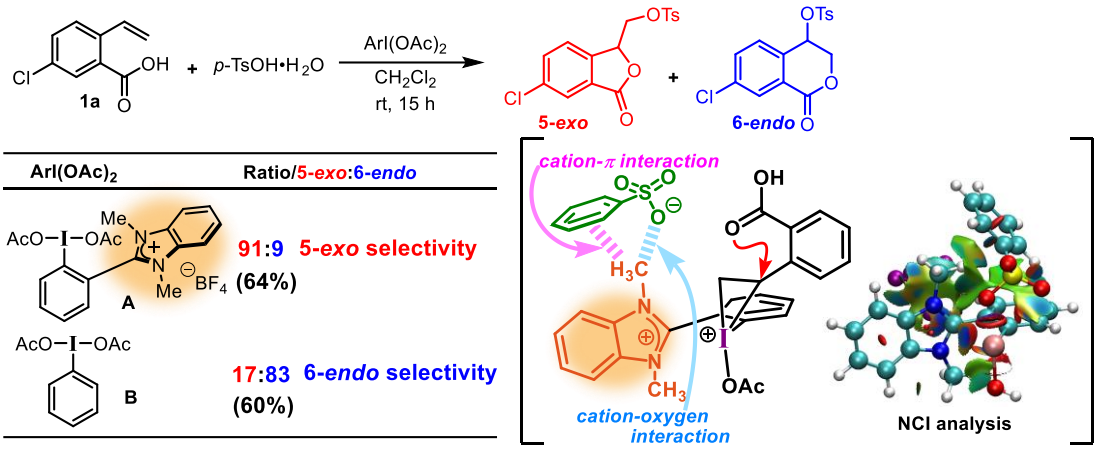
Hypervalent iodines are important non-metal oxidants in organic chemistry and their reactivities are controlled by organic ligands sterically and/or electronically. The sophisticated hypervalent iodines are available for asymmetric reactions, efficient group transfer reactions, and so on.[1] Therefore, an efficient strategy based on a new concept is highly promising even now. In this study, we developed a new methodology using noncovalent interactions derived by cationic heterocyclic substituents on organic framework of hypervalent iodine.

We synthesized hypervalent iodine **A** bearing a benzimidazolium moiety at the ortho position of the iodine atom. For the evaluation of **A**, we chose a model reaction as oxidative tosyloxylactonization of 2-vinylbenzoic acid **1a**.[2] Hypervalent iodine **A** showed 5-*exo* selectivity, while conventional iodobenzene diacetate **B** gave 6-*endo* selectivity. Furthermore, the investigation of various types of substituents revealed that cationic nitrogen-containing heterocyclic moieties close to iodine center was essential to high 5-*exo* selectivity.

Monitoring intermediates and DFT calculation revealed that the regioselectivity was controlled by noncovalent interactions composed of cation-π interaction and cation-oxygen interaction between sulfonate anions and cationic substituents. The trapping of a sulfonate ion retards the intermolecular nucleophilic attack and favors an intramolecular attack leading to the 5-*exo* product.



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