

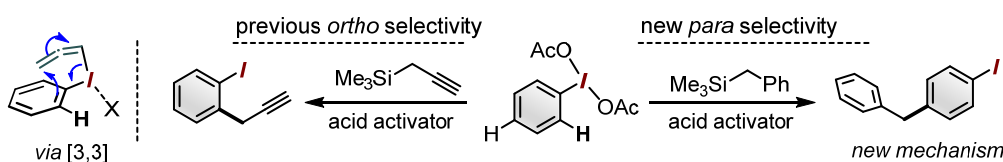
## TOWARDS IODANE-DIRECTED ITERATIVE C-H ALKYLATION

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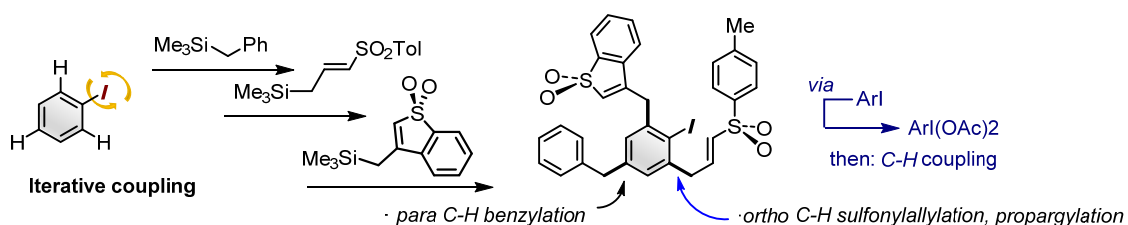
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The synthetic potential of high-valent organoiodine reagents has been the focus of an intense interest. Among the most intriguing reactivity patterns of such reagents is their scarcely utilized ability to undergo iodine-based sigmatropic rearrangement processes resulting in a formal C-H alkylation. Hence, the laboratories of Ochiai and Norton reported a selective formation of the *ortho*-propargyl iodobenzene by treatment of the BF<sub>3</sub>-activated PhI(OAc)<sub>2</sub> with allylsilanes, apparently through a [3,3] sigmatropic rearrangement of an allenyl iodonium intermediate [1]. A greater synthetic potential of this approach to form a broad range of *ortho*-propargyl iodoarenes was recently explored by our laboratory [2]. Although most related studies have centered on *ortho* C-H coupling reactions, we will now discuss an unusual *para*-selective C-H benzylation, achieved by the reaction of acid-activated ArI(OAc)<sub>2</sub> with benzylic silanes.



In addition to discussing the scope and mechanistic details of this reaction, discovered independently by us as well as by Hyatt *et al.*[4], we will also illustrate how iodine re-oxidation allows for the iterative synthesis of multi-substituted iodoarenes cores [3].



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[2] S. Izquierdo, S. Bouvet, Y. Wu, S. Molina, A. Shafir, *Chem. Eur. J.* **2018**, *24*, 15517-15521.

[3] Y. Wu, S. Bouvet, S. Izquierdo, A. Shafir, *Angew. Chem. Int. Ed.* **2019**, *58*, 2617-2621.

[4] C. Mowdawalla, F. Ahmed, T. Li, K. Pham, L. Dave, G. Kim, I. F. D. Hyatt, *Beilstein J. Org. Chem.* **2018**, *14*, 1039-1045