

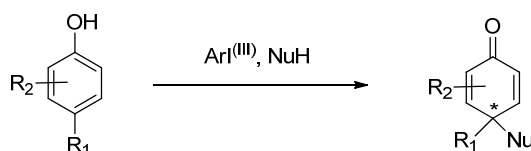
MECHANISTIC STUDIES ON OXIDATIVE DEAROMATIZATION OF PHENOLS PROMOTED BY HYPERVALENT IODINE SPECIES

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Oxidative dearomatization of phenols promoted by hypervalent iodine species coupled with the addition of nucleophiles allows to obtain highly functionalized chiral products that can serve as building blocks for further transformations, such as 1,2- and 1,4-additions, epoxidation, Corey-Chaykovsky, or Diels-Alder reactions. Importantly, this process can be also carried out in the presence of only a catalytic amount of the iodine compound and a stoichiometric terminal oxidant, opening the possibility for an efficient asymmetric catalysis.[1]



Despite the high synthetic importance of the dearomatization of phenols promoted by hypervalent iodine oxidants, there is currently lack of proper understanding of the mechanism of this transformation, which has up to now been a subject of exclusively computational studies.[2] We performed a series of experimental mechanistic investigations to shed light on the pathway that this reaction follows. Our studies, which included: kinetic and voltammetric measurements, characterization of intermediates using EPR and UV/VIS spectroscopy, and radical clock experiments, point to the key role of radical species in the mechanism of the reaction. This finding provides implications for the development of novel synthetic methods based on the dearomatization of phenols with iodine(III) oxidants and have important bearing for the design of novel chiral iodoarene catalysts.

[1] Sun, W.; Li, G.; Hong, L.; Wang, R. *Org. Biomol. Chem.* **2016**, *14*, 2164.

[2] (a) Harned, A. M. *Org. Biomol. Chem.* **2018**, *16*, 2324. (b) Ariafard A., Ganji B. *Org. Biomol. Chem.* **2019**, DOI: 10.1039/C9OB00028C