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## From aminyl radicals to cations. Mechanism switch in Hofmann-Löffler-Freytag-like reactions

Gabrijel Zubčić, Sofia Shkunnikova, Davor Šakić University of Zagreb, Faculty of Pharmacy and Biochemistry

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Ante Kovačića 1, 10000 Zagreb Croatia

Hofmann-Löffler-Freytag (HLF) reaction has seen a resurgence in interest due to shift from metalbased catalysis to organo-catalysis. Recent one-pot approach requires hypervalent iodine compound with source of iodine (I<sub>2</sub> or Nal) for generating radical precursor, that can under UV irradiation form N-centered radical. Rearrangement to a more stable C-centered described.

reaction can be

Iodoarene-Catalyzed Stereospecific Intramolecular sp<sup>3</sup> C–H Amination: Reaction Development and Mechanistic Insights Chendan Zhu,<sup>†</sup> Yong Liang,<sup>‡</sup> Xin Hong,<sup>‡</sup> Heqing Sun,<sup>†</sup> Wei-Yin Sun,<sup>†</sup> K. N. Houk,<sup>\*,‡,§</sup> and Zhuangzhi Shi\*

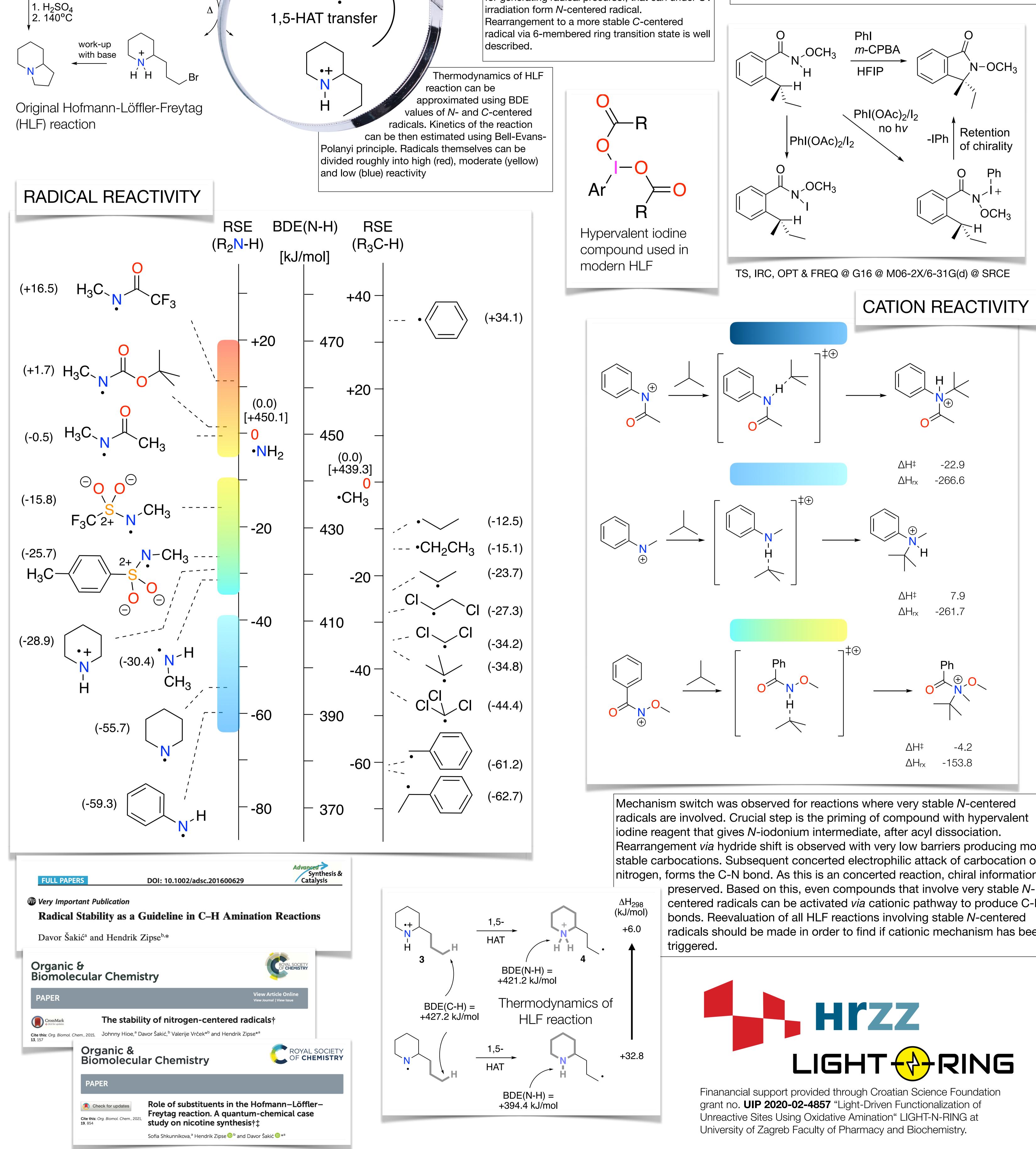
> In recent literature, HLF-like reaction has been observed that proceed to give products with retention of chirality. Using same hypervalent iodine as oxidant, but without source of iodine and without irradiation, this reaction avoids radical mechanism!

DOI: 10.1021/jacs.5b03488

J. Am. Chem. Soc. 2015, 137, 7564–7567

Communication

pubs.acs.org/JACS



 $H_2SO_4$ 

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Rearrangement via hydride shift is observed with very low barriers producing more stable carbocations. Subsequent concerted electrophilic attack of carbocation on nitrogen, forms the C-N bond. As this is an concerted reaction, chiral information is preserved. Based on this, even compounds that involve very stable Ncentered radicals can be activated *via* cationic pathway to produce C-N radicals should be made in order to find if cationic mechanism has been