



PROFESSEUR STÉPHANE QUIDEAU

Université de Bordeaux

Chiral Iodanes in Asymmetric Oxygenative and Carbon-Carbon Bond-Forming Reactions

Mercredi 6 mai 2015, 15h00

Salle D3-2041

Résumé:

The chemistry of hypervalent organoiodine compounds, also referred to as iodanes, has unarguably experienced an impressive development since the early 1990s, as evidenced by both the diversity of iodane reagents that are available today and the number of chemical transformations that these reagents can promote. The initial incitement to the development of λ^3 - and λ^5 -iodanes (*i.e.*, I^{III}- and I^{IV}-based compounds), which was mainly due to their useful oxidizing properties and capacity to replace toxic heavy-metal-based reagents in dehydrogenative and oxygenative reactions, has paved the way to the exploitation of iodanes in various metal-free reactions. Major current and competing research efforts focus on the design of chiral iodane structures for asymmetric synthesis and organoiodine-catalyzed versions thereof.

The focal reaction of our own contributions to this field is the dearomatization of phenols, which constitutes a powerful tactic for the rapid construction of highly functionalized molecular architectures, and often an ultimate key transformation in the biogenesis of numerous natural products. In particular, *ortho*-quinonoid cyclohexadienones can be efficiently generated by iodane-mediated hydroxylative phenol dearomatization (HPD). Such a transformation initially relies on the electrophilic character of the hypervalent iodine center, but it conceptually imposes a subsequent reactivity switch to phenols from being nucleophiles to becoming electrophiles. This "phenolic umpolung" enables regioselective attack of nucleophiles at a substituted *ortho*-carbon center of appropriate starting phenols. Our solutions for selecting the configuration of this carbon center by both substrate- and reagent-controlled iodane-mediated oxygenative phenol dearomatizations, the application of these methodologies in HPD/[4+2] cascade reactions for natural products synthesis, and the extension of the use of our chiral iodanes in asymmetric carbon-carbon bond-forming reactions on phenols and ketones will be presented.

NB: Le département de Chimie de l'Université de Sherbrooke présente chaque année une liste de conférences départementales couvrant tous les domaines de la chimie et dont plusieurs sont rendues possibles grâce à une généreuse contribution de Lundbeck. De plus, le Département de Chimie est fier de s'associer à l'Institut de Chimie du Canada (ICC) afin de présenter quatre conférences annuelles prestigieuses.