Novel Methods for Oxidation of Aromatic Alcohols and Amines: Thermal and Photochemical Pathways

PhD Seminar

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Fri, Feb. 28, 2025
2:00 – 3:00 p.m.
Beaupre Room 105

The selective oxidation of aromatic compounds is a critical transformation in organic synthesis, with applications spanning pharmaceuticals, materials science, and energy systems. Traditional methods often rely on metal-based catalysts, which introduce environmental, economic, and toxicity concerns. In this study, we present a metal-free, cost-effective approach for the oxidation of hydroxymethylated and aminomethylated heteroarenes. Oxidation of hydroxymethylated derivatives is achieved under both thermal and photochemical conditions, whereas aminomethylated compounds have thus far been explored exclusively under thermal conditions.

In thermal oxidation, mild acidic media (5% v/v HOAc or HCl) facilitate the regioselective transformation of acridines, quinolines, pyridines bearing a hydroxymethyl or aminomethyl group to their corresponding aldehydes. For instance, 9-acridinecarboxaldehyde is obtained in quantitative yield using household vinegar at room temperature within three days, or under reflux within two hours without overoxidation to the carboxylic acid. Transformation of indole derivatives is similarly achieved under basic conditions (5% w/v aqueous NaOH).

Mechanistic investigations, including isotope labeling and kinetic isotope effect (KIE) studies (~5 for the rate-limiting C-H bond cleavage), confirm a [1,n] hydride migration (n odd) as the key step, followed by enol tautomerization to give an acridanecarboxaldehyde intermediate. Loss of two hydrogen atom equivalents from this intermediate, presumably to O_2, results in irreversible formation of the product.

Photochemical oxidation of hydroxymethylated aromatic dyes reveals an additional benefit, as the aldehyde formation from anthracenemethanol is coupled with hydrogen gas evolution, suggesting potential applications in solar-driven fuel production. This represents a promising avenue for developing green, sustainable energy sources, integrating small molecule oxidation with hydrogen generation.