New Directions in Organic Electrochemistry

Andrei K. Yudin

University of Toronto
Department of Chemistry
80 St. George Street
Toronto, Ontario
M5S 3H6

General methods for the selective functionalization of hydrocarbons with nitrogen-containing fragments are among the “holy grails” of organic synthesis. Aziridination of olefins is of particular interest due to the enormous synthetic potential of aziridines. Olefin aziridination reactions are usually accomplished *via* metal-mediated transfer of a nitrene fragment to the olefin. The scope of these reactions is often limited to electron-rich substrates. In addition, there have been no examples of catalytic oxidation systems based on readily available oxidants that convert simple amines or amides into active nitrogen transfer species in the presence of olefins and leave no by-products. Our new approach provides an electrochemical solution to this challenge without stoichiometric oxidants. A simple combination of triethylamine, acetic acid, and chemically inert platinum electrodes has led to a highly efficient, room temperature nitrene transfer from *N*-aminophthalimide to a wide range of olefins. Remarkably, both electron-rich and electron-poor olefins are converted to aziridines with high efficiency. Most recently, this methodology was extended to the synthesis of valuable sulfoximines and other nitrogen transfer processes.

We have already used the electrochemically produced aziridines in synthesis and catalysis. For instance, straightforward ring opening with diphenylphosphine has led to versatile P,N ligands that can be obtained in enantiomerically pure form on a multigram scale. The corresponding pyrazole derivatives display high levels of catalytic activity in the challenging area of Suzuki coupling of sterically demanding substrates.

The recently constructed *LightningChem* system is a computer-controlled, automated platform that is being used for parallel organic electrosynthesis. We have demonstrated its utility by making libraries of diamines, α-alkoxycarbamates, α-alkoxyamides, α-alkoxysulfonamides, aziridines, and sulfoximines. We have also shown that modified electrodes can be prepared in this format. Based on our recent findings, optimization of a given electrosynthetic reaction must involve understanding the balance among a number of inter-related variables, such as current density, applied potential, solvent, charge passed, and the nature of electrode. The *LightningChem*™ platform allows for a flexible control of these parameters and is a guide in our future efforts to discover new reactions of broad utility. These and related topics will be discussed.

Selected References:

1. Yudin et al. *J. Am. Chem. Soc.* **2002**, *124*, 530; Chemical & Engineering News (**2002**, January 28th issue, p. 14).
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3. Yudin et al. *Org. Lett.* **2002**, *4*, 2597.