

Metal-Free Carbonylations by Photoredox Catalysis

Category

Organo- and Biocatalysis

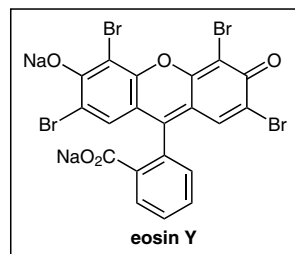
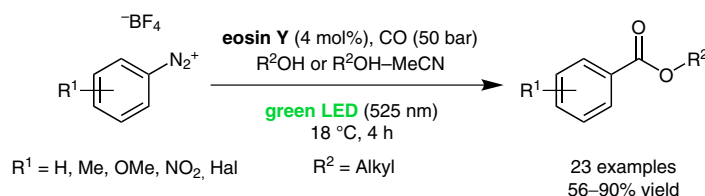
Key words

carbonylation

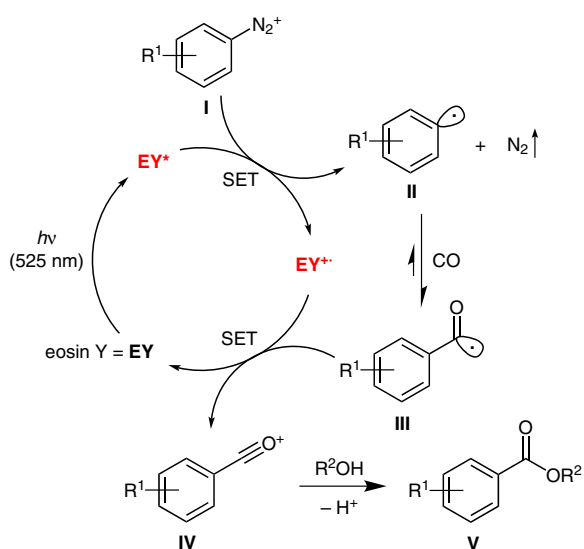
photoredox catalysis

benzoates

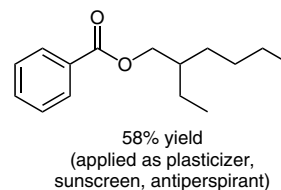
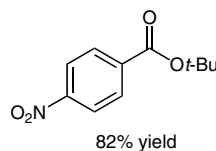
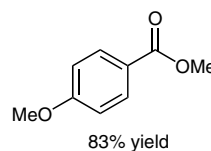
Synfact
of the month



Proposed reaction mechanism:



Selected examples:



Significance: Majek and Jacobi von Wangelin report a photoredox-catalyzed alkoxy carbonylation of arenediazonium salts. The reaction proceeds upon irradiation with green light, in the presence of the corresponding alcohol as solvent, an elevated pressure of CO, and the fluorescein-based dye eosin Y as photosensitizer. A variety of electron-rich and -poor arenediazonium salts served as suitable substrates; this allows the generation of the corresponding alkyl benzoates in good to excellent yields. In contrast to palladium-based carbonylation procedures, this method efficiently gave access to challenging *tert*-butyl benzoates.

Comment: Due to its abundant availability, carbon monoxide is an attractive C₁ building block. While established carbonylation procedures rely on transition metals as catalysts, the authors herein demonstrate the power of photoredox catalysis. Based on experimental data and DFT calculations, a mechanism was proposed that involves a single electron transfer (SET) from the photoexcited dye (EY*) to the arenediazonium ion (I), furnishing aryl radical II after denitrogenation and acyl radical III after subsequent binding to CO. An SET back to EY⁺ gives rise to the highly electrophilic acylium ion IV, which generates benzoate V by addition of the alcohol.