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Title:	Harnessing photo-excited anions in BHAS reactions and mechanistic insights into borrowing hydrogen catalysis.
Authors:	<a href="#">Kundu, Abhishek</a> .
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Abstract:	<p>The synthesis of biaryls bears great importance in organic chemistry, as the unit is seen in a large number of core structural motifs that are found in molecules having tremendous medicinal, agrochemical, and pharmaceutical importance. Henceforth, there is a strong interest in furnishing C–C bonds in biaryls by easily accessible routes. Thus, direct C–H arylation of arenes has gained tremendous attention as it can bypass double preactivation for both participating substrates. In the domain of single electron transfer catalysis, simple organic additives in conjunction with KO t Bu are very effective for facile electron transfer. We have been able to endow transition- metal-free BHAS (Base-promoted homolytic aromatic substitution) protocol that involves commercially available, inexpensive organic molecules to conduct C–C cross-coupling reactions at room temperature under visible light irradiation via a radical pathway. Profound understanding of the initiation pathway reveals multiple initiator species to be responsible for aryl radical generation via single electron transfer. This protocol has been explored successfully in carrying out coupling reactions with various arene partners. Borrowing hydrogen (BH) or hydrogen autotransfer is a multistep catalytic method for the construction of C–C bonds, which consists of consecutive dehydrogenation of alcohol and hydrogenation of in situ generated unsaturated compounds. Hydrogenation of the insitu generated olefin or imine is very crucial step. Series of control experiment including detection of critical reaction intermediates and radical probe experiments, further supported by DFT calculations altogether indicate a radical pathway involving a hydrogen atom transfer step bypassing the intermediacy of metal-hydride species. We have also investigated the origin of solvent dependent chemoselectivity in nitrile hydrogenation via borrowing hydrogen method. The explicit solvent effect involving polar protic isopropanol favors imine metathesis by proton hopping through stepwise addition and elimination steps to produce secondary amine as the final product. The aprotic solvent n-hexane is incapable of such proton migration and inhibits the solvent-assisted imine metathesis to give only primary amines as the final product. This DFT study provides a recipe for the choice of solvents that can dictate chemoselectivity in product formation.</p>
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