

Nucleophile Mediated Addition-Fragmentation Generation of Aryl Radicals from Aryl Diazonium Salts

Authors : Elene Tatunashvili, Bun Chan, Philippe E. Nashar, Christopher S. P. McErlean

Abstract : The reduction of aryl diazonium salts is one of the most efficient ways to generate aryl radicals for use in a wide range of transformations, including Sandmeyer-type reactions, Meerwein arylations of olefins and Gomberg-Bachmann-Hey arylations of heteroaromatic systems. The aryl diazonium species can be reduced electrochemically, by UV irradiation, inner-sphere and outer-sphere single electron transfer processes (SET) from metal salts, SET from photo-excited organic catalysts or fragmentation of adducts with weak bases (acetate, hydroxide, etc.). This paper details an approach for the metal-free reduction of aryl diazonium salts, which facilitates the efficient synthesis of various aromatic compounds under exceedingly mild reaction conditions. By measuring the oxidation potential of a number of organic molecules, a series of nucleophiles were identified that reduce aryl diazonium salts via the addition-fragmentation mechanism. This approach leads to unprecedented operational simplicity: The reactions are very rapid and proceed in the open air; there is no need for external irradiation or heating, and the process is compatible with a large number of radical reactions. We illustrate these advantages by using the addition-fragmentation strategy to regioselectively arylate a series of heterocyclic compounds, to synthesize ketones by arylation of silyl enol ethers, and to synthesize benzothiophene and phenanthrene derivatives by radical annulation reactions.

Keywords : diazonium salts, hantzsch esters, oxygen, radical reactions, synthetic methods

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