

Diazo compounds and oxadiazolines in photochemical reactions for C–C bond formation

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Diazo compounds are versatile reagents commonly applied in the synthesis of small molecules and complex structures, and even pharmaceuticals. Depending on the activation mode, they serve as precursors of various reactive intermediates such as carbenes, metal carbenes, ylides and radicals. Due to low stability, simple diazoalkanes should, however, be generated *in situ* from stable precursors, e.g. 1,3,4-oxadiazolines. Although thermolysis and UV light-mediated photolysis of diazo compounds in the presence of diverse substrates are well known approaches, these reactions generally occur with low selectivity. On the other hand, presence of even traces of metals in products obtained via metal-catalyzed methods limits their application in pharmaceutical industry. Taking into consideration the benefits arising from light-induced strategies, such transformations of diazo compounds bring the attention of organic chemists. Nevertheless, already established methods are limited and mostly targeted at stabilized diazoalkanes.

The aim of this thesis is the design of visible light-induced transformations of diazo compounds and 1,3,4-oxadiazolines leading to new C–C bonds formation. In the first part of my work, I proposed a photochemical allene synthesis from α -aryl- α -diazoesters and propargyl sulfides. Mechanistic experiments confirm that singlet carbenes generated via direct photolysis of diazo compounds are the key intermediates. Next, I have explored yet unknown reactivity of 1,3,4-oxadiazolines upon visible light irradiation. The developed activation mode relies on photoinduced energy transfer from photocatalyst to 1,3,4-oxadiazoline, upon which both triplet carbenes and diazoalkanes are generated. Within this part of my work, I illustrated the utility of proposed activation method with spirocyclopropane synthesis in the presence of electrophilic olefins. Finally, I demonstrated that with the use of porphyrins as photoredox catalysts diazo compounds undergo photochemical transformations under red light irradiation, within which they can serve as precursors or acceptors of reactive intermediates. This was evidenced with the photocatalytic synthesis of oximes, phenantridines and hydrazones.

In summary, I have shown that diazo compounds and 1,3,4-oxadiazolines are reagents of distinct photochemical reactivities, which depending on activation mode give access to various reactive species e.g. carbenes, ylides or radicals.