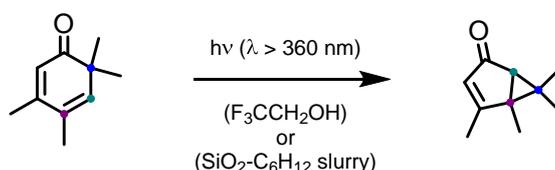


LEWIS-ACID CATALYZED PHOTOREARRANGEMENT OF 2,4-CYCLOHEXADIENONES

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The photochemistry of 2,4-cyclohexadienones first attracted interest as open-chained carboxylic acid derivatives were discovered upon irradiation, a process known as photoacidification. The reaction scope was enhanced by *J. Griffiths* and *H. Hart*, who discovered an altered reactivity of 2,4-cyclohexadienones in polar protic environments, e.g. trifluoroethanol or silica-gel-hexane slurries. They explained the variation of reactivity by a bathochromic shift of the π,π^* transition, obscuring the n,π^* transition assigned to the previously observed α -cleavage [1].



Based on the expertise of Lewis acid induced bathochromic shifts of carbonyl compound in our group [2], we envisioned a photorearrangement reaction, which would proceed with catalytic amount of Lewis acid. UV-Vis measurements with different Lewis acids revealed a significant bathochromic shift of the π,π^* transition up to the visible light region that exceeded the shift in the previously mentioned polar protic reaction media. This shift enabled irradiation of the Lewis-acid-cyclohexadienone complex with visible light. We were pleased to see, that the photorearrangement not only proceeded with stoichiometric amounts of boron trifluoride, but also with catalytic amounts, such as 10 mol% at short reaction times. Syntheses of different 2,4-cyclohexadienones and their photorearrangements were conducted to feature a range of substitution patterns and had high functional group tolerance under our reaction conditions. In addition, triplet quenching experiments were carried out to gain insight into the reactive state.

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[2] a) R. Brimiouille, T. Bach, *Science* **2013**, *342*, 840-843; b) R. Brimiouille, D. Lenhart, M. M. Maturi, T. Bach, *Angew. Chem. Int. Ed.* **2015**, *54*, 3872-3890; c) S. Poplata, T. Bach, *J. Am. Chem. Soc.* **2018**, *140*, 3228-3231; d) S. Stegbauer, T. Bach, *Angew. Chem. Int. Ed.* **2018**, *57*, 14593-14596.