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Chirality and Light: Enantioselective Catalysis of Photochemical Reactions

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Abstract

CHIRALITY AND LIGHT: ENANTIOSELECTIVE CATALYSIS OF PHOTOCHEMICAL REACTIONS

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[2+2] Photocycloaddition reactions belong undisputedly to the most important reaction classes in photochemistry. The creation of up to four new stereogenic centers in a single step and the further use of the formed cyclobutane rings – either directly or after appropriate ring opening – are hallmarks of this powerful transformation. In our group, we have studied two different approaches to achieve a catalytic enantioselective reaction course in [2+2] photocycloaddition reactions. The first approach is based on a triplet energy transfer by hydrogen-bonding chiral catalysts, which in turn are derived from the previously described template 1¹ successfully employed in the total synthesis of (+)-meloscine (2).² The second approach relies on chiral Lewis acids, which change the photophysical parameters of the substrate and allow a selective excitation in the chiral environment, which they provide.

Initial attempts to employ electron transfer or energy transfer for catalytic enantioselective reactions³ have been successfully extended to sensitized [2+2] photocycloaddition reactions.^{4,5} Xanthone **3a** turned out to be an efficient organocatalyst providing good turnover (10 mol%) and high enantioselectivities (>90% ee) in [2+2] photocycloaddition reactions⁴ while thioxanthone **3b** allows for enantioselective reactions promoted by visible light.⁵ Apart from this approach, we have also looked into the possibility of Lewis-acid mediated enantioselectivity in photochemical reactions. Lewis acid **4** was developed for coumarin [2+2] photocycloaddition reactions and is currently being further explored.⁶ The presentation discusses the background of the above-mentioned studies and provides the latest results of our research efforts in this area.

- For recent work, see: a) K. A. B. Austin, E. Herdtweck, T. Bach, Angew. Chem. Int. Ed. 2011, 50, 8416-8419; b) S. C. Coote, T. Bach, J. Am. Chem. Soc. 2013, 135, 14948-14951.
- a) P. Selig, T. Bach, Angew. Chem. Int. Ed. 2008, 47, 5082-5084; b) P. Selig, E. Herdtweck, T. Bach, Chem. Eur. J. 2009, 15, 3509-3525.
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