

CATALYTIC ENANTIOSELECTIVE PHOTOCHEMICAL TRANSFORMATIONS

Reported by Chad Ungarean

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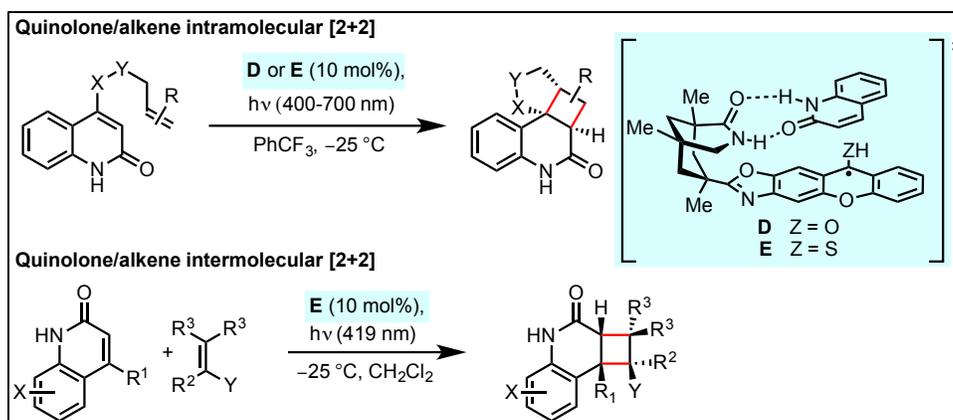
INTRODUCTION

Photochemistry in Nature is a ubiquitous process that plays a role for a myriad of chemical transformations. However, evidence of Nature performing photochemistry on prochiral substrates in a catalytic enantioselective sense has not yet been reported. Thus the ability to develop and utilize catalytic enantioselective photochemical processes would be advantageous for the further expansion of chemical space. New developments in this field include the use of chiral complexing agents through hydrogen bonding as well as utilizing chiral Lewis acids in order to selectively activate the substrate while inducing a chiral environment.

HYDROGEN BONDING CATALYSIS

The Bach group has elegantly developed a chiral scaffold that efficiently interacts with substrates capable of performing

hydrogen bonding (Scheme 1).^{1,2} This system has been utilized for intra- and intermolecular [2+2] cycloadditions with pyridinones and quinolones. The unique catalyst design features a



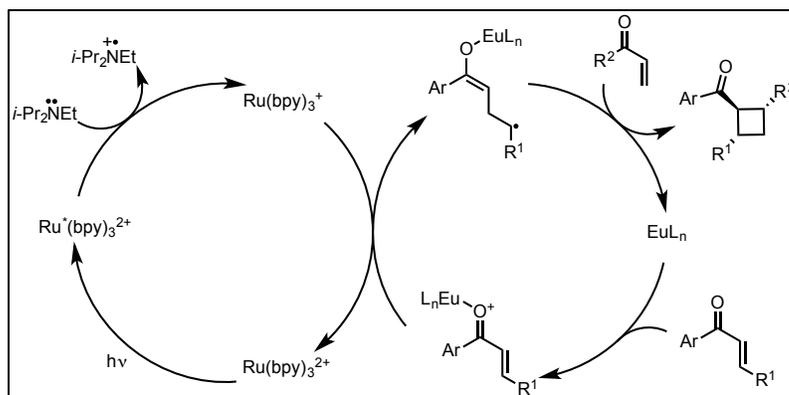
Scheme 1. Examples of [2+2] photocycloadditions using H-bonding catalysis (Bach).

rigid backbone containing a site for hydrogen bonding to the substrate as well as a pendant bifunctional aromatic moiety acting as a photosensitizer and steric component. This methodology has been utilized in the enantioselective syntheses of (+)-meloscine and (-)-pinolinone.^{3,4}

LEWIS ACID MEDIATED CATALYSIS

Introduction of a chiral Lewis acid to substrates capable of direct photoexcitation has proved as a more general approach. Upon coordination of the Lewis acid a bathochromic shift is induced, ultimately differentiating the absorption of the bound substrate in a chiral environment from the unbound substrate. Selection of irradiation wavelength provides preferential excitation of the bound substrate and promotes the reaction with high levels of enantioselectivity. The Bach group has used this concept for the synthesis of (+)-lupinine.⁵

Yoon *et al.* have reported further expansion of this area with the development of a dual catalytic system in which energy transfer from a photosensitizer is specific to the corresponding Lewis acid bound substrate (**Scheme 2**).⁶ The latter methodology has expanded the



Scheme 2. Catalytic cycle of [2+2] photocycloadditions with enones (Yoon).

substrate scope and has shown minimal competitive racemic background reactivity is occurring in the reaction. Furthermore, [2+2] cycloaddition between enones and olefins features reactivity through triplet energy transfer and has provided an efficient platform that may be applied to further chemical transformations.⁷ Further applications of this dual catalytic system is demonstrated in enantioselective [3+2] cycloadditions along with intermolecular conjugate addition of α -amino radicals.^{8,9}

CONCLUSION

Catalytic enantioselective photochemistry provides an entry into uncharted chemical space. While substrate scope and the variety of transformations are still undergoing development, the expansion of this area of catalysis will provide novel disconnections and enable this area to contribute significantly to chemical synthesis.

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