Cation Radical Diels–Alder Reactions via Asymmetric Counteranion-Directed Catalysis

Significance: The Nicewicz group reports both intra- and intermolecular enantioselective Diels–Alder reactions. The photoredox catalyst system consists of a cationic oxopyrylium photooxidant bearing a chiral N-triflyl phosphoramide anion.

Comment: Enantioselective transformations that proceed through a radical ion pair represent a major challenge for asymmetric catalysis. In this report, despite obtaining moderate enantioselectivities, the authors proved the concept by introducing a chiral counteranion. The presented results could provide insights into asymmetric photoredox reactions.

Presented examples:

- 72% yield, dr = 6:1, er = 75:25
- 43% yield, dr = 5:1, er = 73:27
- 63% yield, dr = 6:1, er = 75:25
- 10% yield, dr = 5:1, er = 50:50
- 42% yield, dr = 10:1, er = 50:50

Proposed mechanism:

Intermolecular examples:

- 8% yield, dr > 10:1, er = 75:25
- 85% yield, dr = 8:1, er = 66:34

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DOI: 10.1055/s-0037-1609986; Reg-No.: B03818SF