Photodimerization of Arenediynes

Significance: Cyclic enediynes as well as terminal acyclic enediynes are well known to undergo photochemical C<sub>1</sub>–C<sub>6</sub> cycloaromatization. The authors explored the reactivity of naphthalenyl-substituted arenediynes (1 and 2). While the methoxy-substituted derivative 2 undergoes a photo-Bergman cyclization upon irradiation at 300 nm, 1 shows no formation of C<sub>1</sub>–C<sub>6</sub> or C<sub>1</sub>–C<sub>5</sub> under these conditions. Irradiation of 1 at 350 nm, however, yields a photodimerized product (4).

Comment: The tandem [2+2] photocyclization yields two products in a 4:1 ratio. The structure of the major product (4) was determined by X-ray crystallographic analysis. Based on NMR studies, the authors suggest that the minor product is a diastereomer of 4.