Mechanistic Study on the Regio- and Stereoselectivity in [2+2] Photocycloaddition Reactions of Fran with Cyclic Enones

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[Introduction] The construction of Cyclobutane-ring, a Scheme 1 functional structure, is difficult to construct because of its large strain. However, in the 1960s, the formation of cyclobutane-ring structure was found in the photochemical [2+2] cycloaddition reaction of cyclic enones with alkenes.

Thus, the cyclobutane-ring system can be synthesized by one step (Scheme 1).¹⁻³ In this study, the regio- and stereoselectivity were investigated in a photochemical cycloaddition reactions of 2-cyclopentene-1-one 1a (n = 1) with furan in detail.

[Results]



First of all, the photocycloaddition reaction of **1a** with furan was re-investigated to clarify the

regio- and stereoselectivity in the cyclobutane formation reaction (Scheme 2)⁴. Three isomers, trans-HT2a, trans-HH2a, exo-[2+4], were obtained in a ratio of 9:36:55(47%). The regioselectivity observed in this study was different from that reported previously⁴. Quantum chemical calculations including the intermediary biradicals were performed to understand the observed selectivity (Figure 1).



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[Reference]

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