

Self-Sensitized Diastereodifferentiating *Z-E* Photoisomerization of Chiral Cyclooctene Derivatives possessing a Sensitizer Moiety

キラルなシクロオクテン誘導体の
自己増感ジアステレオ区別 *Z-E* 光異性化

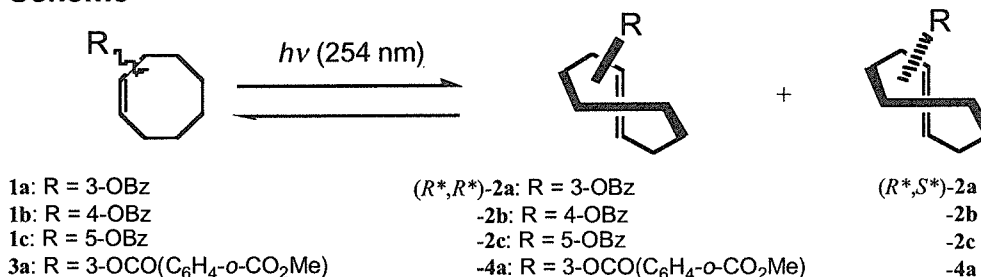
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Unprecedented switching of product chirality occurred in self-sensitized diastereodifferentiating photoisomerization of chiral cyclooctenes tethered to a sensitizer moiety.

Scheme



We prepared three chiral isomers of racemic (*Z*)-3-, 4-, and 5-benzoyloxycyclooctenes (*rac*-**1a–c**), which were subjected to self-sensitizing photoisomerization by irradiating at 254 nm to give the relevant diastereomeric (*E*)-isomer pairs (*R*^{*},*R*^{*})- and (*R*^{*},*S*^{*})-**2a–c** in moderate diastereomeric excesses (de s).

Interestingly, **1a** gave antipodal diastereomers of **2a** at low and high substrate concentration, for which the inverted stereoselectivity upon intra- and

intermolecular sensitizations, dominating respectively at low and high concentrations, are responsible.¹

We further prepared (*Z*)-3-(2-methoxycarbonylbenzoyloxy)cyclooctene (**3a**) as substrate and examined its self-sensitized diastereodifferentiating photoisomerization behavior at varying temperatures. In addition to much enhancement of (*E*)-isomer (**4a**) produced, unusual temperature dependence of the photostationary-state *E/Z* ratio was observed, yielding more strained (*E*)-isomer **4a** at higher temperatures.

The above-mentioned somewhat unexpected behavior of the *E/Z* ratio is inferred to originate from the relatively inefficient intramolecular versus intermolecular sensitization. Detailed mechanisms will be discussed in the presentation.

1) Inoue, T.; Matsuyama, K.; Inoue, Y. *J. Am. Chem. Soc.* **1999**, *121*, 9877-9878.