

Diastereoselective [2+2] Photocycloadditions of Chiral Cyclic Enones to Ethylene in Solution-phase and on Solid-phase**Ken Tsutsumi and Kiyomi Kakiuchi***

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Photochemical [2+2] cycloadditions have come to be seen as valuable reactions in the construction of complex molecules. Despite there being useful applications, far less information about asymmetric photoreactions is known. The most applicable methods for asymmetric synthetic strategies might be diastereodifferentiating photoreactions using chiral auxiliaries. Recently much attention has been paid to solid-phase reactions in synthetic chemistry, because the immobilization of substrates on polymer support results in easier isolation of the product. In addition, a solid-phase reaction sometimes provides a unique product as well as selectivity that may be difficult to achieve by conventional methods. Taking this into consideration, we have studied the diastereoselective [2+2] photocycloaddition of cyclohexenones to the smallest olefin, ethylene, using chiral auxiliaries and the application of polymer-supports to the asymmetric photoreaction.

At first, we investigated the diastereoselective [2+2] photocycloaddition reaction of various chiral cyclohexenones in solution-phase, and found that the (-)-8-arylmethyl groups were more effective chiral auxiliaries.¹ From the detailed examination of reaction conditions, the auxiliary, reaction temperature, solvent, and additive, the highest selectivity (88 % de) was obtained using the (-)-8-(4-nitrophenyl)methyl group.^{1c} Furthermore, the mechanism of the asymmetric induction in the diastereoselective photocycloaddition has been clarified based on spectroscopic examinations.

Next, we synthesized chiral polymer-supported menthols and applied them to the asymmetric photoreaction. Using both polystyrene- and polyethylene glycol-supported menthols as insoluble and soluble polymers in organic solvent, photoreactions proceeded smoothly to give the photocycloadducts.² By using these menthyl auxiliaries, we compared the reactivity and selectivity of photoreactions on solid-phase with those in solution-phase.

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2. Shintani T., Kusabiraki K., Hattori A., Furutani A., Tsutsumi K., Morimoto T., Kakiuchi K., *Tetrahedron Lett.*, 45, 1849-1851, (2004).