THE DEVELOPMENT OF NEW ASYMMETRIC [2+2] PHOTOCYCLOADDITION REACTIONS

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Asymmetric [2+2] photocycloaddition methodology using chiral auxiliaries and chiral additives, is far less developed than other areas of asymmetric synthesis, although a number systems have been studied. For example Piva and Pete recently reported some promising results using chiral hydroxy acids as spacers for controlling asymmetric intramolecular [2+2] photocycloaddition.

Our project involves the diastereoselective intramolecular [2+2] photocycloaddition reactions of alkenols tethered to L-(+)-Valinol derived 3,4,5,6-tetrahydrophthalimides. The basic aim of this project was to develop a new efficient method of asymmetric [2+2] photocycloaddition. THPA undergoes an extremely efficient cycloaddition with either allyl alcohol or propargyl alcohol to form the hydroxycyclobutane anhydride and the hydroxycyclobutene anhydride. We investigated this reaction firstly by using ethanolamines such as (R)-(-)-2-Phenyglycinol and L-(+)-Valinol, in junction with carbonate and silicon tethers, to effect asymmetric [2+2] photocycloaddition.

Intramolecular [2+2] photocycloaddition of allyl alcohol linked to the valinol derivative of 3,4,5,6-Tetrahydrophthalimides either via a carbonate or silicon tether afforded the corresponding cyclobutanes in excellent yield with diastereoselectivites as high as 8:1.

We also investigated the hydrolytic removal of the ethanolamine and L-(+)-Valinol linkers which gave novel access to complex tricyclic lactones via cationic rearrangements.

1. a) M. T.Crimmins and T.L. Reinhold; Org. React., 1993, 44, 297;
   c) H.Herzog, H.Koch, H.-D.Scharf and J.Runsink; Tetrahedron, 1986, 42, 3547;