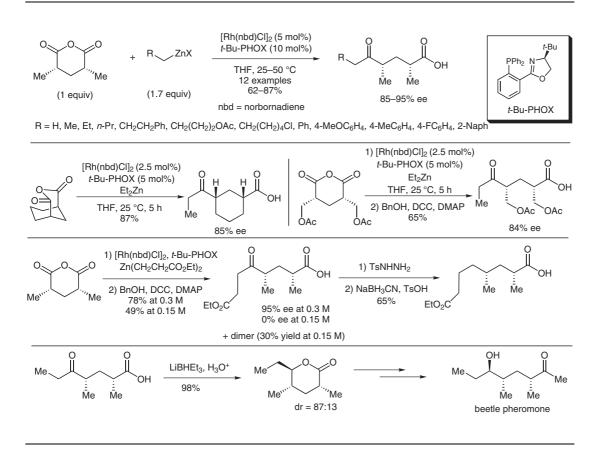
Rhodium-Catalyzed Enantioselective Desymmetrization



Significance: A rhodium-catalyzed enantioselective desymmetrization of various glutaric anhydrides with carbon nucleophiles generates syndeoxypolypropionate synthons in good yields and high ee values. The nucleophiles are commercially available or in situ generated alkyl or benzyl zinc reagents; aryl nucleophiles, however, are not compatible. A good range of alkyl nucleophiles, including those with an ester or chloride moiety, is shown. Electron-rich benzylic nucleophiles result in lower ee values due to a background reaction. Some examples of post-modifications of the product are also provided, including a deoxygenation and a diastereoselective reduction producing an intermediate to the synthesis of a beetle pheromone.

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Comment: The *syn*-deoxypolypropionate unit is a useful synthon in organic synthesis and the present paper provides a novel method to generate enantioenriched varieties of this unit. One particular example with a zinc homoenolate sheds light on the reaction mechanism. This example gives the desired product and a dimer resulting from isomerization of the nucleophile. The dimer can be reduced at higher concentrations, which suggests that the zinc nucleophile and rhodium interact before addition to the anhydride.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

rhodium

zinc

enantioselective desymmetrization

syn-deoxypolypropionate

