Stereoselective Reduction of the Ketone Group in α-Allyl β-Keto Esters

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Abstract—Stereoselective reduction of the ketone carbonyl group in α-allyl-substituted β-keto esters with sodium tetrahydridoborate in the presence of 2 equiv of $MnCl_2$ quantitatively afforded the corresponding *syn*-isomeric alcohols. The reduction of the same substrates with L-selectride [$LiBH(s\text{-}Bu)_3$] in anhydrous THF was characterized by low chemoselectivity, and *anti*-isomeric alcohols were formed in about 50% yield. Under analogous conditions, α-allyl ketones smoothly reacted with L-selectride to give *syn*-isomeric alcohols in quantitative yield. The corresponding *anti* isomers were synthesized by the Mitsunobu reaction of the *syn* isomers with formic acid, followed by alkaline hydrolysis.

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