Category

Metal-Mediated Synthesis

Ate Complexes of Secondary Boronic Esters as Chiral Organometallic-Type Nucleophiles for Asymmetric Synthesis *J. Am. Chem. Soc.* **2011**, *133*, 16794–16797.

Boron-Ate Complexes as Chiral Nucleophiles for Asymmetric Synthesis

 $\begin{aligned} &\text{Ar} = 4\text{-MeOC}_6 H_4, \ 3,5\text{-}(\text{CF}_3)_2 \text{C}_6 H_3 \\ &\text{R}^1 = \text{Ar}, \ \text{Ar-substituted Alk} \\ &\text{R}^2 = \text{Me}, \ \text{Et}, \ \dot{\textbf{F}} \text{Bu}, \ \text{allyl}, \ \text{substituted Alk} \\ &\text{E} = \text{various electrophiles} \end{aligned}$

Selected examples:

NHCO₂Bn 80% yield 85% yield 66% yield 100% es 100% es 92% es E = N-iodosuccinimide E = N-bromosuccinimide E = dibenzyl azodicarboxylate $Ar = 4-MeOC_6H_4$ $Ar = 3,5-(CF_3)_2C_6H_3$ $Ar = 3,5-(CF_3)_2C_6H_3$ CO₂t-Bu 4-MeOC₆H 98% yield 61% yield 84% yield 100% es 100% es 98% es E = tropylium tetrafluoroborate E = trichloroisocyanuric acid E = trichloroisocyanuric acid $Ar = 4-MeOC_6H_4$ $Ar = 3,5-(CF_3)_2C_6H_3$ $Ar = 3,5-(CF_3)_2C_6H_3$

Significance: The authors report that secondary chiral boronic esters can be converted into reactive nucleophiles by addition of an aryllithium reagent. These enantiomerically enriched nucleophiles react with a broad range of electrophiles with inversion of stereochemistry.

Comment: By changing the substituents on the aryl group on boron, a switch in mechanism from a classical 2e⁻ pathway (nucleophilic substitution) to a radical pathway was observed. Therefore, electron-poor boronic esters favor the desired nucleophilic substitution, whereas electron-rich esters give racemized products.

SYNFACTS Contributors: Paul Knochel, Andreas K. Steib Synfacts 2012, 8(1), 0077 Published online: 19.12.2011 **DOI:** 10.1055/s-0031-1289458; **Reg-No.:** P15311SF