



1,3-Dienylboronates in Diels-Alder Reactions: Part II¹

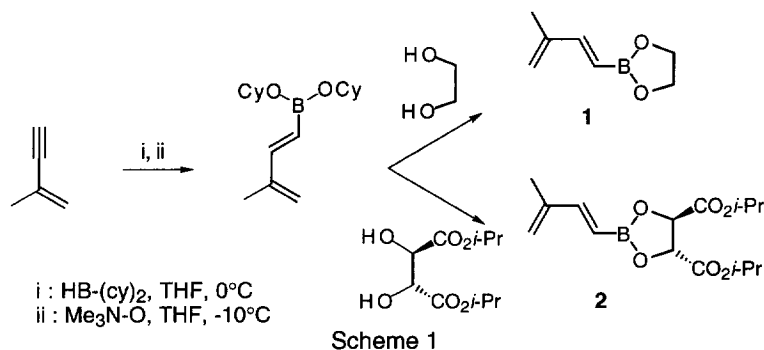
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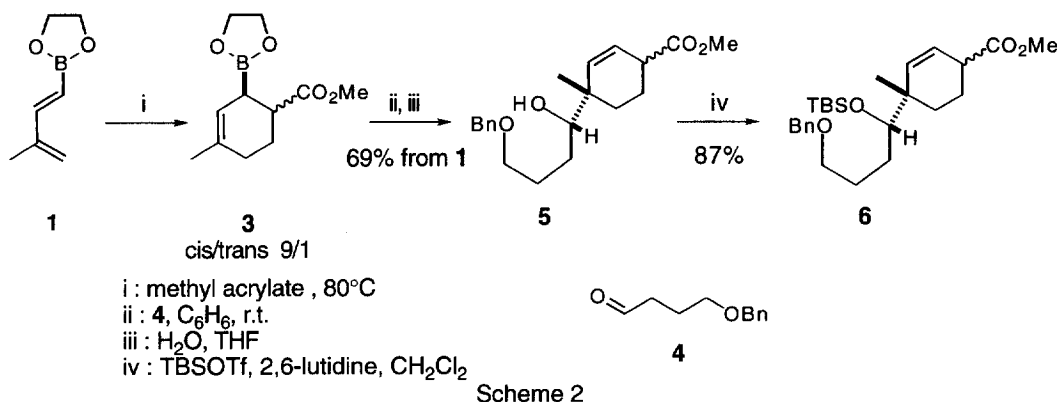
Abstract: The first asymmetric tandem reaction involving a 1,3-dienylboronate derived from tartrate esters as the diene proceeds with an enantiomeric excess of 70%. Copyright © 1996 Published by Elsevier Science Ltd

Cycloaddition reactions involving 1,3-dienylboronates as dienes open a wide field of synthetic applications due to the high reactivity of the thus obtained allyl boronate adduct.³ Consequently, it would be highly interesting to develop an enantiocontrolled version of this reaction. However, the two reported examples in the literature were not encouraging: even when the cycloaddition reaction was performed with sterically hindered enantiomerically pure 1,3-dienylboronates from pinene derived and *N*-phenyl maleimide, only the racemic mixture has been isolated.⁴ The only means which has been found to achieve some asymmetric induction deals with a diene bearing a chiral quaternarized boramine⁴ in which the reactivity of boron atom has been considerably reduced.

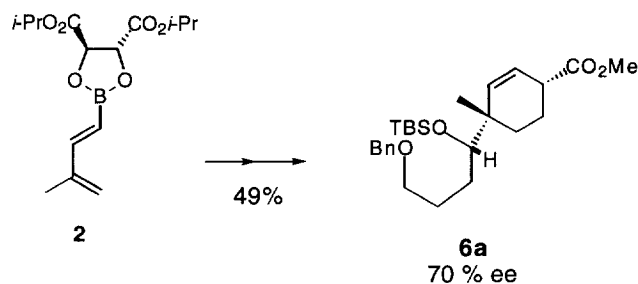
We therefore focussed our efforts on the synthesis of an enantiomerically pure 1,3-dienylboronate from tartrate esters derived which have been shown to induce asymmetry not only through steric hindrance, but mainly through stereoelectronic effects.⁵ We thus decided to investigate the use of sterically hindered tartrates: 1,3-dienylboronates **1** and **2**, which have been synthesized in 80 and 76% yield respectively from 3-methyl-3-butene-1-yne *via* an already described three step one pot procedure (scheme 1).⁶



In order to study the synthetic potential of these tartrate ester derivatives, we first tried the cycloaddition/allylboration cascade as depicted in scheme 2, involving the achiral boronate **1**. Addition was performed using methylacrylate as a dienophile, without solvent, at 80°C for 16 hours. Allylboronate **3** was obtained as a 9/1 diastereoisomeric mixture. This crude material which proved to be sensitive to acids, water and air, was directly treated with aldehyde **4**, and yields after hydrolysis the alcohols **5** (69% overall yield from **1**). In order to limit the presence of minor impurities, **5** was silylated (87% yield). Resulting ester **6** was isolated as the same 9/1 mixture of diastereoisomers, in agreement with a fully controlled reaction of intermediate allylboronate in the presence of an aldehyde.^{1,6}



The same tandem reaction (steps i-iv) was performed on enantiomerically pure **2** (scheme 3), and yielded a 9/1 diastereoisomeric mixture of silylated compound **6**, which were impossible to separate. NMR analysis using chiral europium shift reagent showed **6a** as the major diastereoisomer (estimated yield 49% from **2**) to be composed of a 85/15 mixture of enantiomers (ee = 70%).



We have thus demonstrated that cycloaddition reaction of a chiral 1,3-dienylboronate bearing a tartrate ester moiety on boron atom is possible. Improvement of the enantiomeric excess using lower reaction temperatures and catalytic Lewis acids are currently in progress, and will be reported in due time.

References and Notes

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