1,4-Elimination of Allylic Boronic Esters towards Substituted 1,3-Dienes with an Unusual Silyloxy Leaving Group

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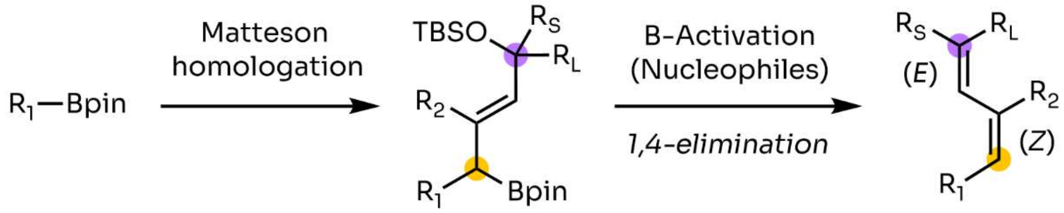
There are a plethora of olefination reactions involving boronic esters known to literature, with the Zweifel olefination and boron-Wittig-type reactions being prominent examples. [1-3] While 1,4-eliminations are generally underexplored in synthesis, the use of boronic esters in these reactions is not documented to date.

Herein we describe the first method for the synthesis of terminal and internal dienes by 1,4-elimination of allylic boronic esters. The combination of the Matteson homologation of boronic esters and subsequent introduction of a vinyllithium nucleophile, bearing an allylic silyl ether, yields the necessary substrates. The elimination proceeds after activation of the boronic ester with alkoxide or organolithium nucleophiles. Silanolate is expelled as an unusual leaving group simultaneously forming both double bonds with excellent selectivities. While (E)-vinyllithium nucleophiles result in (1Z,3E)-dienes, the corresponding (Z)-isomers lead to the (1E,3E)-products. The mechanism and selectivity of the reaction were further elucidated with DFT-calculations. With the possibility of iteratively introducing stereogenic centers by Matteson homologations followed by the presented 1,4-elimination complex polyketide fragments of natural products bearing highly substituted dienes should be easily accessible.



- Yields up to 80 % (2 steps)
- *Z*- and *E*-Selectivities up to 99:1
- (1*E*,3*E*)-dienes with (*Z*)-Allyl boronic esters

[1] Boron-Wittig-Reaction: G. Cainelli, G. Dal Bello, G. Zubiani, *Tetrahedron Lett.*, **1966**, *7*, 4315; A. Pelter, E. Buss, E. Colclough, *J. Chem. Soc. Chem. Commun.*, **1987**, 297.
[2] Zweifel-Olefination: G. Zweifel, H. Arzoumanian, C. C. Whitney, *J. Am. Chem. Soc.*, **1967**, *89*, 3652; R. J. Armstrong, V. K. Aggarwal, *Synthesis*, **2017**, *49*, 3323.
[3] Review: K. Bojaryn, C. Hirschhäuser, *Chem. Eur. J.*, **2022**, *28*, e20210412.