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Synthesis and Cycloaddition of 2-(Dialkoxyboryl)-1,3-butadiene

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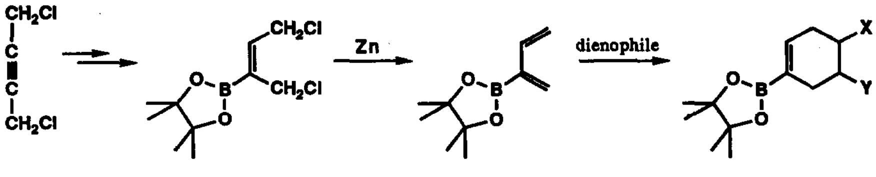
Abstract: A two-step procedure for the synthesis of a pinacol ester of (1,3-butadien-2-yl)boronic acid **2** from 1,4-dichloro-2-butyne is reported. The boronate **2** is found to be an extremely reactive diene for the Diels-Alder reaction to produce functionalized cyclic 1-alkenylboronates in high yields.

Alicyclic 1-alkenylboron compounds are easily accessible by hydroboration of alkynes and are widely used species for the synthesis of a host of unsaturated organic compounds.[1] However, the synthetic methods for cyclic 1-alkenylboron derivatives are very rare and the known examples require several steps with low total yields. Herein, we wish to report a simple two-step procedure for the synthesis of a pinacol ester of (1,3-butadien-2-yl)boronic acid **2** *via* the hydroboration-reductive dechlorination of 1,4-dichloro-2-butyne. The utility of the new boron reagent is demonstrated by the synthesis of six-membered cycloalkenylboron compounds **3** *via* the Diels-Alder cycloaddition reaction (Eq. 1).

The hydroboration of 1,4-dichloro-2-butyne with diisopinocamphenylborane[2] and the dealkylation with excess acetaldehyde are followed by the ester exchange with pinacol to produce **1** in 88 % yield (Bp 82 °C/0.08 mmHg). The title compound is readily synthesized by treating this boronate with activated zinc dust in THF. The boronate thus obtained is highly susceptible to dimerization, but the quick trap-to-trap distillation in high vacuo allows the isolation of almost pure **2** in a range of 50 to 70% yields.[3]



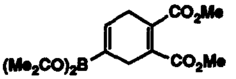
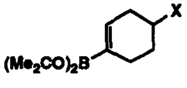
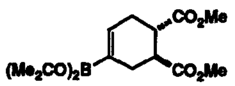
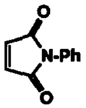
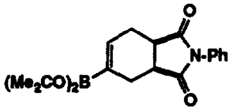
1 **2** **3**

(1)

The cycloaddition of **2** to common dienophiles is summarized in Table 1. Surprisingly, this diene is considerably more reactive than the common dienes for the Diels-Alder reaction.[4] The reaction proceeds even at room temperature or more generally at 50 °C to produce pure adducts with the representative alkene and alkyne dienophiles. Singleton and Vaultier have recently noted the exceptional high regioselectivity and reactivity of ethenylboranes or boronates as dienophiles for the Diels-Alder reaction.[5] Although **2** shows only weak directing effects for methyl acrylate (entry 2), the cycloadditions to acrolein and methyl vinyl ketone produce 1,4-disubstituted isomers regioselectively (entries 3 and 4).

The present study provides a new access to cycloalkenylboronic esters which can not be achieved using conventional hydroboration techniques. The reaction conditions for cycloaddition are sufficiently mild enough to permit various structural variations, thus, the synthetic applications for numerous reactions[1] reported in boron chemistry are anticipated.

Table 1. Cycloaddition Reaction of **2** to Dienophiles[a]

Entry	Dienophile	Equivs	Product		Yield (%)
1	$MeO_2C-C\equiv C-CO_2Me$	10			55
2	$CH_2=CHCO_2Me$	10		$X=CO_2Me$	31 (6:4)[b]
3	$CH_2=CHCHO$	10		$X=CHO$	81
4	$CH_2=CHCOMe$	10		$X=COMe$	72
5	(E)-$MeO_2CCH=CHCO_2Me$	3			70
6		2			94

[a] A mixture of **2** and dienophile (2-10 equivs) in toluene was stirred at 50 °C for 10 h. The products were isolated by Kugelrohr distillation or chromatography over Florisil.

[b] Oxidation with alkaline hydrogen peroxide gave a mixture of 4- and 3-carbomethoxycyclohexanones.

References and Notes

1) A. Pelter, K. Smith and H. C. Brown, "*Borane Reagents*", Academic Press, New York (1988).

2) We appreciate Professor M. Vaultier for sending us a detailed manuscript for the synthesis of vinylboronates *via* the hydroboration-dealkylation technique using diisopinocamphenylborane.[5c]

3) To the suspension of zinc powder (5.3 g) activated by 1,2-dibromoethane (0.35 ml) in THF (6 ml) was added a solution of **1** (8 mmol) in THF (6 ml). After stirring for 1 h, the mixture was diluted with hexane, filtered through celite, washed with brine, and finally dried over $MgSO_4$ in the presence of small amounts of phenotiazine. The distillation in a trap cooled to 0 °C gave **2** in 50-70 % yields (the bath temperature, 20-35 °C / 0.01mmHg). The boronate **2** is highly susceptible to dimerization, thus the concentrated residue should be distilled quickly without delay.

4) W. Carruthers, "*Cycloaddition Reactions in Organic Synthesis,*" Pergamon Press, New York (1990).

5) (a) D. A. Singleton and J. P. Martinez, *J. Am. Chem. Soc.*, **112**, 7423 (1990). (b) D. A. Singleton, *Ibid.*, **114**, 6563 (1992). (c) P. Martinez-Fresneda and M. Vaultier, *Tetrahedron Lett.*, **30**, 2929 (1989); (d) N. Noiret, A. Youssofi, B. Carboni and M. Vaultier, *J. Chem. Soc., Chem. Commun.*, **1992**, 1105 and references therein.

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