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A Simple, General and Stereoselective Synthesis of 1-(Dialkoxyboryl)-1,3-Dienes.

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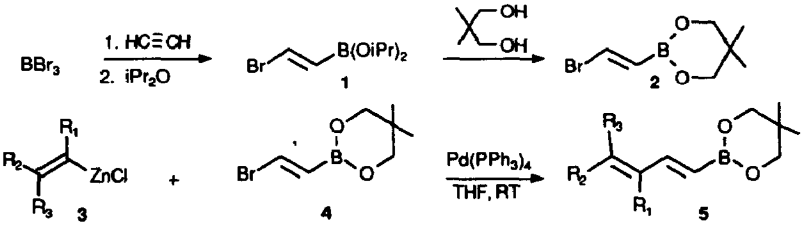
Abstract : A simple, general and highly stereoselective synthesis of 1-dialkoxylboryl-1,3-dienes that involves a palladium (0) catalyzed cross-coupling reaction of the boronic ester **4** derived from (E)-2-bromoethenylboronic acid and 2,2-dimethyl-1,3-propanediol with various alkenylzinc chlorides is described.

Despite the wide variety of 1,3-dienes used in the Diels-Alder cycloaddition reaction [2,3], only a few examples explore the advantage of a metallic substitution like silicon [4], tin [5], or boron [6] containing groups, which would offer opportunities for further transformations. Of particular interest are 1-dialkoxyboryl-1,3-dienes since they have been shown to be reactive partners in the Diels-Alder reaction leading to stereodefined cyclohexenyl boronates **2** which are also allylboronates. A tandem sequence : [4 + 2] cycloaddition followed by the allylboration of an aldehyde would therefore lead to cyclohexenyl alcohols with the control of the newly created stereocenters [7].

The value of such a sequence would be magnified if a simple stereoselective and general route to 1-(dialkoxyboryl)-1,3-dienes of type **1** were available. Until now, these dienylboronates were prepared by hydroboration of enynes [7] which is not a general route to these compounds. We now report such a synthesis.



The (E)-bromoethenylboronate **1** is accessible by bromoboration of acetylene [8] followed by esterification of the resulting E-2-bromoethenyldibromoborane with iPr$_2$O [9]. Transesterification with 2,2-dimethyl-1,3-propanediol (DMPG) gave the air stable boronate **2** in a 80 % yield after distillation (**2** ≥ 99 % isomeric purity by capillary GC.). The vinylboronate **1** is a useful precursor for the synthesis of (E)-olefins by the stepwise cross-coupling reactions with organozinc chlorides and then with organic halides in the presence of a base, both catalyzed by palladium complex [10]. However, the 1,3-dienylboronates, which have to be intermediates in these couplings, were not isolated. We thought that the use of air stable boronates derived from DMPG or pinacol would facilitate the isolation and purification of **5**. Hence, the reaction of vinylzinc chlorides **3** with **4** in the presence of a catalytic amount of Pd (PPh$_3$)$_4$ (1 %) in THF at room temperature for 6 h leads to the 1-(dialkoxyboryl)-1,3-dienes **5**. Results are reported in the table.

It can be seen from this table that the method leads to a variety of dienes in good yields. The stereochemical integrity of both the vinylzinc chlorides and the (E)-bromoboronate **2** is maintained during the coupling process in agreement with literature results [11], thus allowing the access to [E,E] and [Z,E]-1,3-dienylboronic esters. It is also worth noting that functional groups can be introduced on the dienyl frame like the trimethylsilyl (entries 5 and 6) or alkoxy substituents (entries 8, 9 and 10) and most probably many other, since the presence of a carbon-zinc bonds on a substrate is compatible with a large number of functionalities [12]. Work is in progress along these lines in our laboratories.

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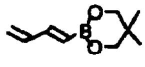
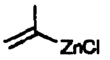
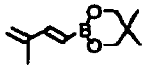
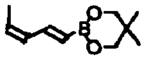
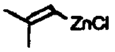
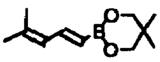
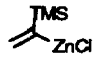
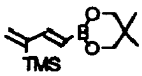
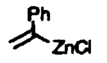
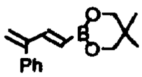
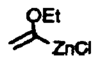
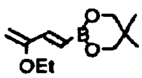
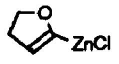
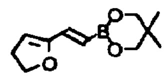
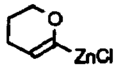
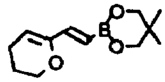
Table : Synthesis of 1,3-Dienylboronic esters 5.

Entry	Organozinc Reagent	Product	N°	Yield %[(a)]
1			5a	51
2			5b	79
3			5c	72
4			5d	65
5			5e	82
6			5f	79
7			5g	67
8			5h	62
9			5i	63
10			5j	66

(a) : yields are for isolated pure products.

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