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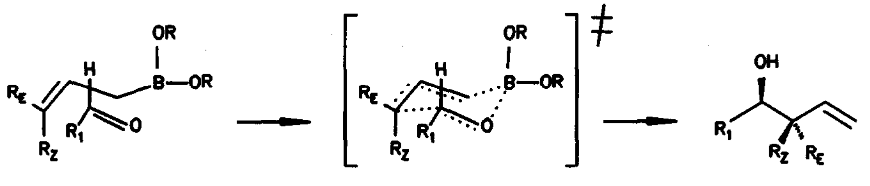
Allylboronic Ester Synthesis: A Mechanistic Study

George W. Kabalka* and R. David Pace

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

Abstract: The selective formation of allylboronic esters via the allylation of trialkylborates using allylmagnesium bromide was found to be temperature dependent. At -78°C, allylmagnesium bromide reacts cleanly with triisopropylborate to provide allyldiisopropoxyborane. The initially formed bromomagnesium allyl triisopropoxyboronate precipates at this temperature prohibiting the formation of more highly allylated products.

Allylboron reagents are playing an increasingly important role in organic synthesis. Allylboron reactions with carbonyl compounds are, for example, highly diastereoselective yielding products possessing contiguous stereogenic centers. Typically, optically active auxiliaries attached to the boron dictate the diastereofacial selectivity. However substrate controlled allyl- and crotylborations recently have been achieved giving rise to exceptional diastereoselectivities (1).



The typical method for preparing allylboronic acid involves the addition of allylmagnesium bromide to a trialkylborate followed by hydrolysis. However, little is known concerning the factors responsible for the selective nature of this addition reaction although a recent report has appeared that describes the preparation of borinic esters via the addition of alkylmagnesium halides to trialkylborates (2). Apparently, the reaction of allylmagnesium halides is mediated by the stability of the bromomagnesium dialkyldialkoxyborate.

Two methods are generally utilized for the preparation of allylboronic esters. One method involves the simultaneous addition of the Grignard reagent and the trialkylborate (3). In a second method, an equimolar quantity of Grignard is added to trialkylborate (4). We examined the latter method due to its relative simplicity and often superior results. We wish to report the results of a study focused on the formation of allylboron reagents.

All reactions were carried out in ether utilizing equimolar quantities of reagents. Good yields of allyldiisopropoxyborane were obtained from the reaction of allylmagnesium bromide with triisopropylborate which was precooled to -78 °C (Table 1, entries 6-8). In all cases, the reaction mixtures were analyzed by comparing the

Table 1. Temperature Dependence

$$B(O\mathit{i}Pr)_3 \xrightarrow[\text{2. } H^+]{\text{1. AllMgBr}} \underset{\mathbf{1}}{B(O\mathit{i}Pr)_3} + \underset{\mathbf{2}}{AllB(O\mathit{i}Pr)_2} + \underset{\mathbf{3}}{All_2BO\mathit{i}Pr} + \underset{\mathbf{4}}{All_3B}$$

Entry	Temp. °C		Product Distribution, %				Rxn Time, hr
	AllMgBr	B(O*i*Pr)$_3$	1	2	3	4	
1[d]	RT	RT	79	2	17	2	1.0
2[d]	RT	0	63	0	37	0	1.0
3[d]	RT	0	59	0	41	0	2.0
4[d]	0	0	64	0	36	0	1.0
5	RT	-40	49	13	38	0	1.0
6	RT	-78	13	87	0	0	1.0
7	RT	-78	11	87	2	0	6.0
8[b]	RT	-78	18	82	0	0	0.5
9	-78	-78	6	91	3	0	0.5
10	-78	-78	4	94	2	0	0.5
11[b]	-78	-78	6	94	0	0	0.5
12[b]	-78	-78	4	96	0	0	3.0

[a]Reactions were quenched at 0°C except as noted. [b]Quenched at -78 °C. [c]Intensity of ^{11}B-NMR peaks.
[d]No precipitate formed over course of the reaction.

relative intensities of the ^{11}B peaks (2). The yield of the monoallylation product increased further when the Grignard reagent was precooled to -78 degrees prior to its addition to the triisopropylborate (entries 9-12). In all reactions carried out at -78 °C (entries 6-12), a thick white precipitate of triisopropoxyallylbornate formed during the addition of Grignard reagent which dissolved on warming the reaction mixture to 0 °C. To minimize equilibration reactions (entries 8,11, and 12) anhydrous HCl (1.2 *M* in ether) was added at -78 °C prior to warming.

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