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9-ALLENYL-9-BBN : A NEW REAGENT FOR THE EFFICIENT ALLENYLBORATION OF CARBONYL COMPOUNDS PRODUCING THE HOMOPROPARGYLIC ALCOHOLS IN HIGH PURITY AND YIELD

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Abstract: A new reagent, 9-allenyl-9-BBN (1), has been developed for the convenient and efficient synthesis of a variety of homopropargylic alcohols via the allenylboration of aldehydes and ketones.

Homopropargylic alcohols serve as valuable intermediates in organic synthesis.[3] A number of methods are available for the synthesis of these intermediates involving allenyl- or propargylorganometallics (M= Mg, Li, Ti, Zn, Al, Sn, Si and B).[4] However, many of these methods are impractical on a large scale and suffer from a variety of problems. For instance, allenylmagnesium bromide reacts with carbonyl compounds rather nonselectively, and provides the corresponding homopropargylic alcohols in poor yields. With hindered ketones, the reagent provides a mixture of propargylic and allenic alcohols.[4a,b] Favre and Gaudemar have shown that allenylboronate esters react with aldehydes to provide the corresponding homopropargylic alcohols. However, with hindered ketones, this reagent provides a mixture of homopropargylic and allenic alcohols.[4n,o] Further, these reactions also require a higher temperature and longer reaction times. Consequently, there is a need for an efficient, regio- and chemoselective allenylborating agent.

In this communication, we wish to report the synthesis of such a new reagent, 9-allenyl-9-BBN (1), which undergoes a facile condensation with a representative aldehydes and ketones to provide homopropargylic alcohols in excellent isolated yields (Scheme I).

Scheme I

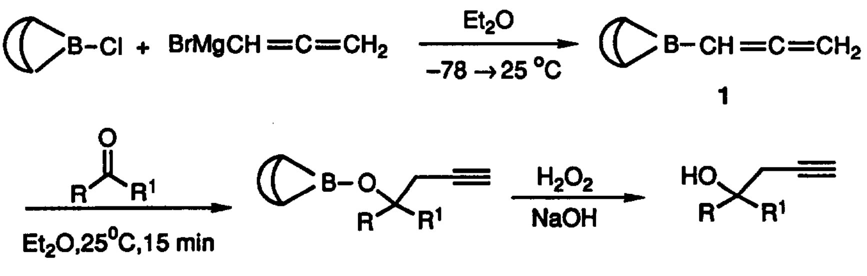
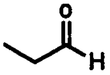
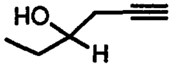
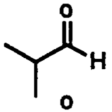
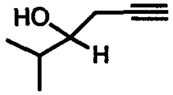
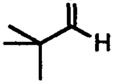
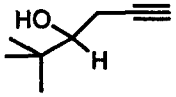
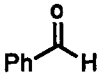
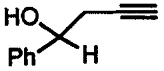
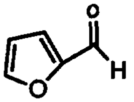
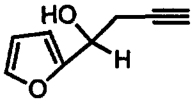
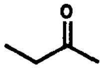
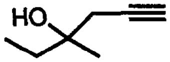
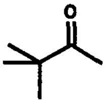
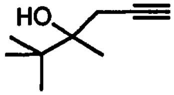
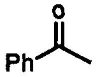
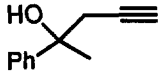
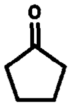
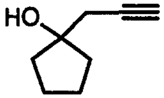
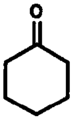
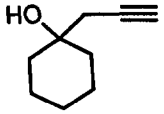


Table I summarizes the results of allenylboration of representative carbonyl compounds with **1** at 25 °C in Et_2O. As is clear from the table, 9-allenyl-9-BBN (**1**) reacts with both aldehydes and ketones to provide the corresponding homopropargylic alcohols in 79-89% yields.

Table I. Allenylboration of Representative Carbonyl Compounds with B-Allenyl-9-BBN (1)[a]

entry	carbonyl compound	homopropargylic alcohol[b]	% yield[c]
1			82
2			88
3			89
4			82
5			79
6			89
7			88[d]
8			86
9			87
10			88

[a] Reactions were carried out at 25 °C in Et_2O for 15 min. [b] Isolated yields of pure products. [c] Characterised by ^1H, ^{13}C and IR spectra. [d] Reaction required 90 min for completion.

9-Allenyl-9-BBN (**1**) posseses several advantages. It can be very easily prepared and stored (under nitrogen) for long periods of time without any detectable change.[5a] The allenylborations of carbonyl compounds with **1** can be precisely and conveniently monitored by ^{11}B NMR spectroscopy.[5b]

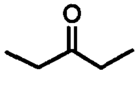
The value of 9-allenyl-9-BBN (**1**) is further evident by its highly regioselective allenylborations of ketones such as diethyl ketone (**4**) and *t*-butyl methyl ketone (**5**), as compared to the behavior of allenylmagnesium bromide (**2**) and di(*n*-butyl) allenylboronate (**3**)

= = —MgBr

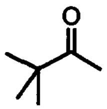
2

= = —B(O*n*-Bu)$_2$

3



4



5

Table II summarizes these results. While the allenylation of **4** with **2** affords 88% of the homopropargylic alcohol and up to 12% of the undesired allenic alcohol, the allenylation of **4** with **3** affords only 41% of the desired product and 59% of the isomeric allenic alcohol. The results of allenylation of *t*-butyl methyl ketone (**5**) are similar. Thus, the allenylations of **5** with **2** and **3** provide 27% and 60% of the undesired allenic alcohol respectively. In marked contrast, the allenylboration of **4** and **5** with 9-allenyl-9-BBN (**1**) produces the homopropargylic alcohols exclusively.

Table II. A Comparison of the Allenylborations of 4 and 5 with the Reagents 1-3

			% product alcohol	
entry	ketone	reagent	homopropargylic	allenic
1	**4**	**2**	88	12[a,b]
2	**4**	**3**	41	59[c]
3	**4**	**1**	100	0
4	**5**	**2**	73	27[a,b]
5	**5**	**3**	40	60[c]
6	**5**	**1**	100	0

[a] Determined by ^{1}H NMR. [b] Only 60-70% conversion. [c] From ref. 4o.

The following procedure is representative for the synthesis of homopropargylic alcohols with 9-allenyl-9-BBN (**1**). To a stirred solution of 9-chloro-9-BBN (6.2 g, 40 mmol) in ether (40 mL), allenylmagnesium bromide in ether (40 mL, 1.0 M, 40 mmol) was added at –78 °C, under nitrogen.[6] After 30 min, the mixture was allowed to warm to room temperature and stirred for 1 h. Then, stirring was discontinued to allow Mg^{+2}

salts to settle, and the clear supernatant layer was transferred into another flask. Following evaporation of the ether (14 mm, 1 h), the residue was distilled to obtain pure 9-allenyl-9-BBN (**1**) as a colorless liquid. bp. 69 ^{o}C/0.5 mm; yield, 4.8 g (75%). Next, cyclohexanone (0.98 g, 10 mmol) in ether (10mL) was added dropwise at 25 ^{o}C to the solution of 9-allenyl-9-BBN (1.6 g, 10 mmol) in ether (10 mL). The reaction mixture was stirred for 15 min and then oxidized with alkaline hydrogen peroxide. Following the usual workup procedure, 1-cyclohexyl-3-pentyne-1-ol[41] (1.20 g, 88 %) was isolated in pure form.

Presently, we are exploring the chemo-, regio-, and stereoselectivities of this new reagent in the allenylboration of carbonyl compounds. These results will be reported soon.

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References and Notes

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5. (a) 9-Allenyl-9-BBN (**1**) was stored as a 1.0 M solution in ether under nitrogen at 0 ^{o}C, and its chemical purity was monitored by ^{11}B NMR spectroscopy, with time. The reagent was observed to be highly stable under these conditions with no detectable change noted over one month. (b) In ^{11}B NMR, 9-allenyl-9-BBN (**1**) in ether appears at δ 79 ppm. However, as the allenylboration proceeds, the borinate product appears at δ 52 ppm.

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