Organoboranes for Synthesis. 15. *B*-Allenyl-9-BBN: A Highly Regiospecific and Chemoselective Reagent for Allenylboration of Representative Carbonyl Compounds, Leading to Homopropargylic Alcohols and Amines

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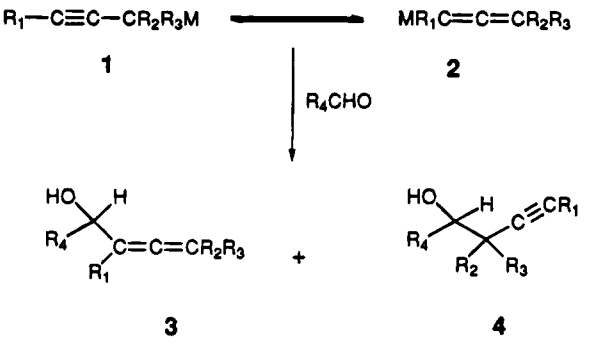
Reactions of *B*-allenyl-9-BBN (**11**) with representative carbonyl compounds, such as aldehydes, ketones, acid chlorides, carboxylic acid esters, and imines, proceed cleanly with the allenyl moiety undergoing transfer to the carbonyl or imine carbon, with allenic to propargylic rearrangement, and the boron moiety to the carbonyl oxygen or imine nitrogen. A simple oxidation with alkaline hydrogen peroxide results in the formation of the corresponding homopropargylic alcohols and amines in excellent yields. Aldehydes, ketones, and imines react in a 1:1 stoichiometry, while acid chlorides and carboxylic acid esters react with 2 equiv of the reagent. The relative reactivities of representative aldehydes, ketones, and esters toward **11** were also explored. Besides being highly regiospecific, the reagent **11** also possesses a remarkable chemoselectivity. *B*-Allenyl-9-BBN can distinguish between less and more sterically hindered aldehydes, ketones, and esters, making possible the clean and selective propargylboration of a desired carbonyl group in complex organic molecules containing less reactive functional groups.

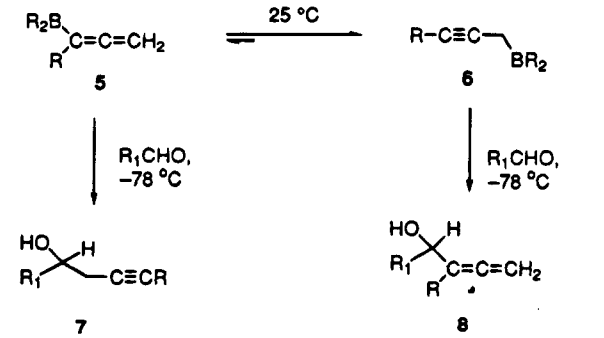
Homopropargylic and α-allenic alcohols are valuable intermediates in organic synthesis as these structural units are present in a variety of natural products and biologically active compounds.[2] Synthesis of these compounds is generally accomplished by reactions involving propargylic (**1**) or allenic (**2**) anion equivalents.[3] The utility of organometallic derivatives of types **1** and **2** in such a methodology is unfortunately limited due to their ambident nucleophilic nature allowing them to react with electrophiles unselectively to produce a mixture of allenic (**3**) and acetylenic (**4**) products (Scheme 1). Furthermore, the presence of other functional groups, such as esters or nitriles, in the substrate is not tolerated by these organometallics, restricting the use of these reagents in the total synthesis of complex natural products.

Allenic and propargylic organometallic reagents using an array of metals (Mg, Li, Ti, Zn, Al, Sn, Si, B) have been tested in recent years for regiospecific synthesis of allenic (**3**) and homopropargylic (**4**) alcohols, and it has been established that they react with aldehydes with variable regioselectivity affording mixtures of **3** and **4**.[3a] The use of organoboranes in organic synthesis as both

Scheme 1



Scheme 2



reactive and selective reagents has been amply demonstrated.[4] Zwiefel *et al.* reported a boron-based reagent (**5**–**6**), obtained from lithium chloropropargylide and trialkylborane, for the synthesis of homopropargylic (**7**) and α-allenic alcohols (**8**) selectively by controlling the reaction temperature (Scheme 2).[5]

Unfortunately, this method is useful only for the synthesis of substituted homopropargylic and allenic

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alcohols. Wang *et al.* prepared trimethylsilyl-substituted α-allenic alcohols (**8**, R = TMS) using *B*-[γ-(trimethylsilyl)propargyl]-9-BBN.[6] This method is also applicable only for the synthesis of α-substituted allenic alcohols. Even though considerable effort has been devoted to the synthesis of unsubstituted homopropargylic alcohols **7** (R = H), which are versatile intermediates in the synthesis of various natural products, only a limited number of methods are available in literatutre. Although allenylmagnesium bromide is commonly used for the synthesis of unsubstituted homopropargylic alcohols with aldehydes, its reactions always suffer from poor yields. A serious disadvantage of this reagent is that it gives a mixture of homopropargylic and allenic alcohols with hindered ketones.[7] Of the other reported reagents, allenyl di(*n*-butyl)boronate also reacts selectively with aldehydes, but furnishes a mixture of products with ketones.[8] Allenylsilanes,[9] triisopropyl-substituted propargylic lithium reagent,[10] and the corresponding Reformatsky reagent[11] have been shown to react with aldehydes and with some ketones selectively. However, there is a need for a reagent which is easy to prepare and is highly regio- and chemoselective with various carbonyl compounds. Our interest in this area has led to the discovery of a new reagent *B*-allenyl-9-BBN (**11**), readily prepared from *B*-chloro-9-BBN (**9**) and allenylmagnesium bromide (**10**). Our preliminary studies showed that this reagent, in contrast to the previously known reagents described above, undergoes a facile condensation with representative aldehydes and ketones and provides exclusively the corresponding homopropargylic alcohols in excellent yields.[12] In continuation of this study, we decided to systematically explore the reactivity of this reagent toward other functional groups, such as acid chlorides, esters, imines, etc. It is gratifying to observe that this reagent indeed reacts cleanly with many functional groups and affords the corresponding homopropargylic alcohols and amines in excellent yields and isomeric purities. More importantly, *B*-allenyl-9-BBN preferentially reacts with aldehydes in the presence of ketones and esters and can even distinguish the less sterically hindered aldehydes or ketones from the more sterically hindered, a selectivity which has not been hitherto demonstrated with other reagents.

Results and Discussion

B-Allenyl-9-BBN (**11**) is easily prepared in one step starting from *B*-chloro-9-BBN (**9**)[13] and allenylmagnesium bromide (**10**)[14] in excellent yield. Alternatively, it can also be prepared from *B*-methoxy-9-BBN and **10**. The latter method suffers from low yields of the product, and therefore, we prefered to use the first method (eq 1).

Scheme 3

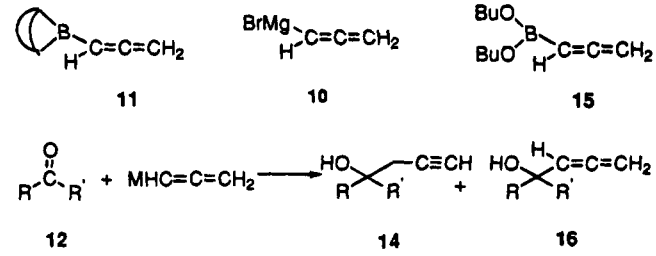
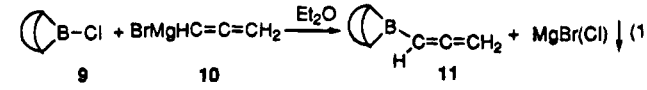


Table 1. Comparison of the Allenylboration of Diethyl and *tert*-Butyl Methyl Ketone with Reagents 11, 10, and 15

ketone	reagent	14[a] (%)	16 (%)
diethyl ketone	**11**	100	0
	10	88	12[b]
	15	41	59[c]
tert-butyl methyl ketone	**11**	100	0
	10	73	27[b]
	15	40	60[c]

[a] Determined by ^{1}H NMR. [b] Only 60–70% conversion. [c] From ref 8b.



The reagent **11**, prepared by this method, can be distilled and stored either in neat condition or as a 1 M solution in hexane at 0 °C under a nitrogen atmosphere. This reagent is highly stable, and no changes are observed in the ^{11}B NMR spectrum even after a long period of time. Diethyl ether was selected as the best solvent for allenylborations of carbonyl compounds based on our earlier experience with allylboration reactions.[15]

It must be pointed out that *B*-allenyl-9-BBN undergoes highly regioselective allenylborations of both simple and hindered ketones, such as diethyl ketone (**12h**) and *tert*-butyl methyl ketone (**12g**), as compared to the other reagents, such as allenylmagnesium bromide (**10**) and dibutyl allenylboronate (**15**, Scheme 3, Table 1).

Thus, allenylation of diethyl ketone (**12k**) with **10** gives 88% homopropargylic alcohol **14k** and 12% of the allenic alcohol **16k**. The same reaction with **15** provides only 41% of the homopropargylic alcohol along with 59% of the allenic alcohol. Our reagent **11** provides only homopropargylic alcohols exclusively. The results of the allenylation of *tert*-butyl methyl ketone (**12g**) are similar. Similarly, the reagents **10** and **15** provide with **12g** only 73% and 40% of the homopropargylic alcohols, respectively. In contrast, *B*-allenyl-9-BBN (**11**) gives essentially the corresponding homopropargylic alcohol exclusively.

Allenylboration of Aldehydes and Ketones. Allenylboration of aldehydes and ketones with *B*-allenyl-9-BBN results in the formation of the corresponding borinate esters **13**, which under the usual alkaline hydrogen peroxide oxidation conditions afford homopropargylic alcohols **14** cleanly (Scheme 4). In a typical allenylboration experiment, aldehyde in diethyl ether (1 M solution) was added to a solution of **11** in ether (1 M solution) at room temperature. The reaction was com-

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Scheme 4

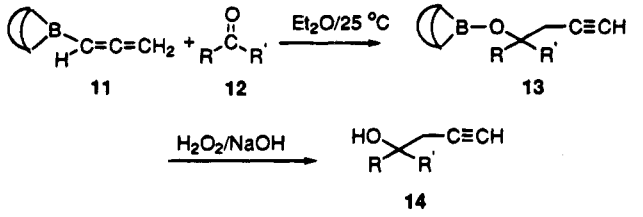

Table 2. Allenylboration of Representative Aldehydes (RCHO) and Ketones (RCOR')

R	R'	yield[a] (%)
C_2H_5	H (**12a**)	**14a** (82)
$(CH_3)_2CH$	H (**12b**)	**14b** (88)
$(CH_3)_3C$	H (**12c**)	**14c** (89)
Ph	H (**12d**)	**14d** (82)
2-furyl	H (**12e**)	**14e** (79)
C_2H_5	CH_3 (**12f**)	**14f** (89)
$(CH_3)_3C$	CH_3 (**12g**)	**14g** (88)[b]
Ph	CH_3 (**12h**)	**14h** (86)
Ph	Ph (**12i**)	**14i** (90)
CH_2=CH	CH_3 (**12j**)	**14j** (71)
C_2H_5	C_2H_5 (**12k**)	**14k** (87)
cyclohexanone (**12l**)		**14l** (87)
cyclopentanone (**12m**)		**14m** (88)

[a] Isolated yield of the product. The reaction is complete in <5 min. [b] Reaction required 90 min for completion.

plete in less than 5 min according to ^{11}B NMR, which showed a single peak at δ 57 ppm corresponding to the product borinate ester **13**. The reaction thus proceeds under mild conditions with excellent yields. The regioselectivity of this reagent in producing homopropargylic alcohols selectively even with hindered aldehydes and ketones is unprecedented. The only isolated product from this reaction after workup is the corresponding homopropargylic alcohol, since 1,5-cyclooctanediol, resulting from the oxidation of 9-BBN, is highly soluble in water and, therefore, can be easily washed away.

Table 2 summarizes the results of allenylboration of aldehydes and ketones with reagent **11**. The allenylboration of aldehydes and unhindered ketones is usually instantaneous at room temperature. The reaction is quite rapid even with less reactive ketones, such as benzophenone. However, *tert*-butyl methyl ketone is a lone exception as its reaction is slow and requires 1.5 h for completion at room temperature, as indicated by ^{11}B NMR. As the reaction of **11** with aldehydes and ketones is instantaneous at room temperature, we decided to investigate the reactivity of the reagent **11** at lower temperatures with a typical aromatic aldehyde, PhCHO (**12d**), and a typical aromatic ketone, $PhCOCH_3$ (**12h**). The reagent was added to a solution of **12d** and **12h** in ether separately at −78 °C, and the reaction was checked for its completion by adding a reactive aldehyde, such as acetaldehyde, in excess at different time intervals. Oxidation followed by GC analysis of the product mixture was used to determine the time required for the completion of the reaction. In the case of PhCHO, the reaction was complete in <5 min, and in the case of $PhCOCH_3$, the reaction was complete in 2 h, both at −78 °C. Thus, the difference in the rate of the reaction of *B*-allenyl-9-BBN with PhCHO and $PhCOCH_3$ is significant. This observation led us to explore the chemoselectivity of the reagent **11** with different pairs of carbonyl compounds of variable reactivity.

Unlike trialkylboranes, *B*-allenyl-9-BBN reacts with α,β-unsaturated carbonyl compounds in 1,2-fashion exclusively, similar to the behavior of dialkylallylboranes. In the case of vinyl methyl ketone, the reagent **11** adds in 1,2-fashion to give the corresponding homopropargylic alcohol.

Scheme 5

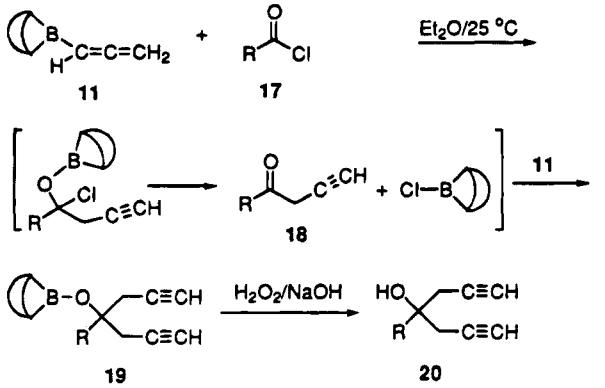

Table 3. Allenylboration of Acid Chlorides (RCOCl)

R	product	yield[a] (%)
CH_3	**20a**	72
Ph	**20b**	76

[a] Isolated yield of the product.

Allenylboration of Acid Chlorides. We have previously reported the reactions of *B*-allyl-9-BBN with various electrophiles.[16] Reactions of *B*-allenyl-9-BBN exhibited a similar pattern of behavior in its reactions with electrophiles. In addition, in the case of *B*-allenyl-9-BBN, we have determined the regioselectivity with less reactive electrophiles. With reagent **11**, the reaction of acid chlorides **17a** and **17b** was complete within 30 min at room temperature, affording after oxidative workup tertiary alcohols **20a** and **20b**. In this reaction 2 mol of allenylborane are consumed per molecule of the acid chloride.

This reaction can be rationalized as indicated in Scheme 5. It appears that the first mole of **11** reacts with acid chloride to form the intermediate ketone **18**, which reacts instantaneously with a second mole of *B*-allenyl-9-BBN to furnish the tertiary alcohol **20** after oxidative workup of the intermediate borinate **19**. This is further evident from the generation of *B*-chloro-9-BBN (^{11}B NMR at δ 27 ppm in ether) in the reaction mixture after 30 min. The ratio of borinate to *B*-chloro-9-BBN in the ^{11}B NMR spectrum is 1:1. The rate of the reaction of the intermediate ketone **18** with the reagent **11** is instantaneous, and hence, we were unable to stop the reaction at this stage. Table 3 summarizes the results obtained from this reaction. Both acetyl chloride and benzoyl chloride react with 2 equiv of the reagent **11** in ether to furnish the corresponding tertiary alcohols cleanly in excellent yields without any contamination of allenic side products.

Allenylboration of Imines. Allenylboration of imines can be expected to form the corresponding homopropargylic amines. Indeed, *B*-allenyl-9-BBN reacts vigorously with imines at room temperature, and the reaction goes to completion within 15 min (Scheme 6). The ^1H NMR spectrum of the product indicates the presence of a small amount (2−4%) of the corresponding allenic amine (**23**), along with a major product, homopropargylic amine (**22**) (Table 4).

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Scheme 6

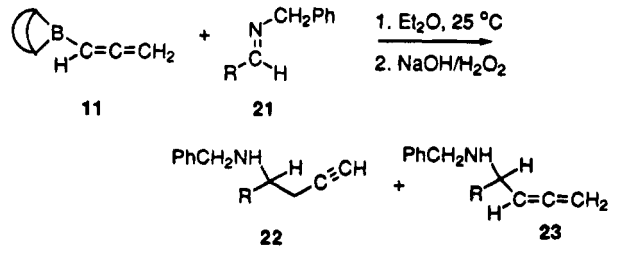
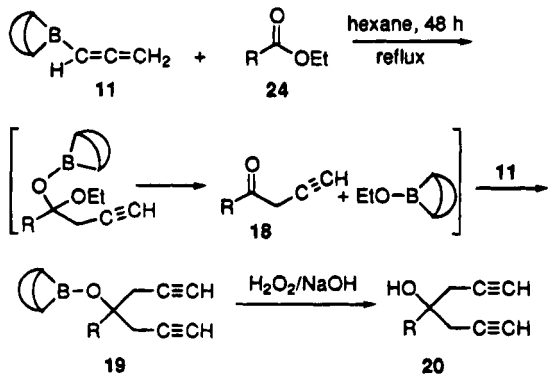


Table 4. Allenylboration of Imines ($RCH{=}NCH_2Ph$)

R	product **22** (**23**)[a]	yield[b] (%)
$(CH_3)_2CH$	**22a**, 96 (4)	90
Ph	**22b**, 98 (2)	84

[a] Ratios are based on ^1H NMR. [b] Overall isolated yield of the product.

Scheme 7



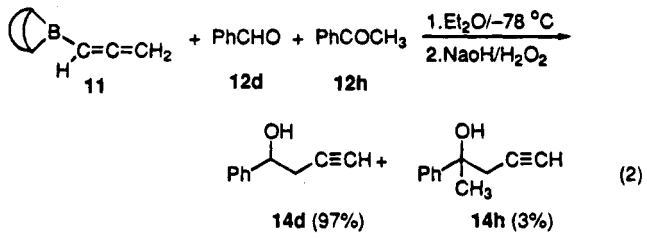
The addition of allylboranes and boronates to imines has been studied by Yamamoto *et al.* They established that the reaction of *B*-allyl- and *B*-crotyl-9-BBN derivatives with chiral amines proceeds with very high 1,2- and 1,3-asymmetric induction.[17] They also reported the addition of allenic organometallic compounds with imines.[18] These results suggest that a good diastereoselectivity could be expected in the addition of *B*-allenyl-9-BBN to chiral imines, a simple way to synthesize chiral homopropargylic amines. This work is in progress in our laboratories.

Allenylboration of Carboxylic Acid Esters. *B*-Allenyl-9-BBN reacts much more slowly with esters compared to the other carbonyl derivatives discussed earlier. No reaction was observed between ethyl acetate (**24**, R = CH_3) and **11** at room temperature, either in ether or in hexane, even with prolonged reaction times. However, the reaction is complete in refluxing hexane in 48 h. Along with the expected diacetylenic tertiary alcohol (**20**), side products having allenic structures were also formed in a considerable amount (15%) (Scheme 7).

Reaction with ethyl benzoate was even more sluggish. Only 15% of the conversion was observed even after refluxing in hexane for 8 days. *tert*-Amides and alkyl halides also proved to be inert toward *B*-allenyl-9-BBN.

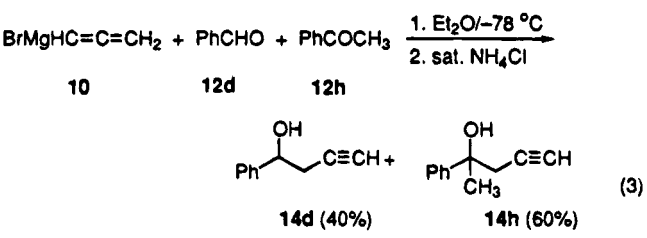
Chemoselectivity Studies of *B*-Allenyl-9-BBN. It is clear from our low-temperature experiments of **11** with **12d** and **12h** that the reagent *B*-allenyl-9-BBN reacts faster with aldehydes than with ketones, especially at −78 °C. This prompted us to explore the chemoselectivity of this reagent toward such compounds. Since allenylmagnesium bromide is a widely used reagent for the synthesis of homopropargylic alcohols, we compared the chemoselectivities of representative carbonyl compounds with *B*-allenyl-9-BBN and the corresponding allenylmagnesium bromide to examine the advantage of reagent **11**. The following experiments for the selectivity studies were performed.

B-Allenyl-9-BBN (**11**) was added to an equimolar mixture of PhCHO and $PhCOCH_3$ in ether (0.4 M solution) at −78 °C and stirred for 4 h. At the end of 4 h, an excess of a highly reactive aldehyde, such as acetaldehyde, was added to the reaction mixture, and the mixture was warmed to the room temperature. The reaction mixture was then oxidized, and the products were analyzed by GC using an internal standard (*n*-undecane). The complete absence of a product from acetaldehyde and *B*-allenyl-9-BBN confirmed a 100% reaction of **11** to **12d** and **12h** before the acetaldehyde addition to the reaction mixture. GC analysis showed 97% of the product from PhCHO (**14d**) and 3% of product from $PhCOCH_3$ (**14h**) indicating the excellent chemoselectivity of this reagent (eq 2).



(2)

Similarly, allenylmagnesium bromide (**10**) was added to a solution of PhCHO and $PhCOCH_3$ (1:1 mixture) in ether at −78 °C and stirred for 4 h. The reaction mixture was brought to room temperature after addition of excess acetaldehyde at −78 °C and quenching with saturated NH_4Cl solution. The organic phase was dried over anhydrous Na_2SO_4, and the products were analyzed by GC. In this case, the product formed from PhCHO is 40% and that from $PhCOCH_3$ is 60%, indicating that the allenylmagnesium bromide does not descriminate between aldehydes and ketones.



(3)

These results clearly demonstrate the superior chemoselectivity of the reagent **11.** On the other hand, allenylmagnesium bromide exhibits relatively poor selectivity under comparable reaction conditions.

Other pairs of carbonyl compounds selected for chemoselectivity studies included aldehydes (simple and hindered)/ketones, aldehydes/esters, five-membered/six-membered cyclic ketones, and cyclic/acyclic ketones. These reactions were performed at different temperatures to examine the suitable conditions for the best chemoselectivity of the reagent, and the results are summarized in Table 5. It is evident from the results

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Table 5. Reactivities of Different Carbonyl Compounds toward 11 in Et_2O[a]

carbonyl compds	product	temp (°C) (reaction time (h))	% product with **11**[b]	% product with **10**[b]
benzaldehyde	**14d**	−78 (4)	97	40
acetophenone	**14h**		3	60
pivalaldehyde[c]	**14c**	0 (0.5)	98	
tert-butyl methyl ketone	**14g**		2	
benzaldehyde	**14d**	25 (0.5)	100	81
ethyl benzoate	**20b**		0	9[d]
cyclohexanone	**14l**	−78 (4)	87	65
cyclopentanone	**14m**		13	35
diethyl ketone	**14k**	−78 (4)	99	48
cyclohexanone	**14l**		1	52
cyclohexanone	**14l**	−78(4)	96	45
tert-butyl methyl ketone	**14g**		4	55
cyclopentanone	**14m**	−25 (4)	79	51
tert-butyl methyl ketone	**14g**		21	49
acetophenone	**14h**	−78 (4)[e]	100	80
benzophenone	**14i**		0	20

[a] The reaction mixture was 0.4 M, both in substrate and in reagent **11**. [b] Determined by GC from response ratios determined for authentic samples. [c] Product from aldehyde in this reaction with **10** was not clean. [d] Product obtained in this reaction is **20b**. [e] Mole % of product formed in this reaction with **11** were same even at room temperature.

that aldehydes are much more reactive than ketones (eq 2). Carboxylic acid esters exhibit no reactivity toward **11** in the presence of benzaldehyde (0:100) at room temperature. Cyclohexanone reacts faster than cyclopentanone (87:13), and cyclic ketones are more reactive toward **11** compared to acyclic ketones [diethyl ketone: cyclohexanone (1:99), *tert*-butyl methyl ketone:cyclohexanone (4:96), *tert*-butyl methyl ketone:cyclopentanone (21:79)]. For comparison, the same pairs of carbonyl compounds were also examined with allenylmagnesium bromide, and the results established that the Grignard reagent is much less chemoselective.

Conclusions

The allenylboration of carbonyl compounds with *B*-allenyl-9-BBN (**11**) provides an excellent method for the synthesis of homopropargylic alcohols with high regioselectivity. This reagent possesses several advantages over the other available reagents. It is easy to prepare and can be stored under nitrogen over a long period of time. It is highly reactive, and the rate can be conveniently monitored using ^{11}B NMR spectroscopy; the workup procedure is simple and furnishes products directly with very high purity. Reaction of reagent **11** with imines provides the corresponding homopropargylic amines with high regioselectivity. Reagent **11** reacts with acid chlorides and esters to yield the corresponding tertiary alcohols. *B*-Allenyl-9-BBN is a versatile reagent, reacting readily with a variety of functional groups, and yet is able to distinguish very well between different carbonyl compounds. It is not only highly regiospecific in its reactions with carbonyl compounds but is highly chemoselective in nature. This reagent can selectively react with aldehydes in the presence of ketones and esters. Thus, *B*-allenyl-9-BBN is a reagent of choice for allenylboration and in general for the synthesis of homopropargylic alcohols and amines.

Experimental Section

All glassware was dried at 150 °C for at least 12 h, assembled hot, and cooled under a purge of nitrogen. Special techniques for handling air-sensitive materials are described elsewhere.[19] All solvents were distilled over LAH and stored under nitrogen. 9-BBN dimer was purchased from Aldrich Chemical Co. and used as such. Propargyl bromide (Aldrich), carbonyl compounds (Aldrich), and *n*-undecane (Phillips Petroleum Co.) were obtained and used without further purification. HCl in ether was prepared using Brown[2] apparatus. ^1H NMR spectra were recorded at 300 MHz, while all ^{13}C NMR spectra were recorded at 75.5 MHz in $CDCl_3$ with TMS as an internal standard. Chemical shifts for ^1H NMR are reported as parts per million (ppm) downfield from TMS and for ^{11}B NMR are reported as parts per million (ppm) downfield from $BF_3{\cdot}OEt_2$. Boiling points reported are uncorrected. Chemoselectivity studies were done using internal standard method from the response ratios determined for authentic samples.

Preparation of *B*-Allenyl-9-BBN (11). Allenylmagnesium bromide in ether (40 mL, 1.0 M, 40 mmol) was added dropwise to a well-stirred solution of *B*-chloro-9-BBN (6.2 g in 40 mL ether, 40 mmol) at -78 °C. Following the completion of addition, the reaction mixture was vigorously stirred for 30 min at −78 °C and was allowed to warm to room temperature. Stirring was discontinued after 1 h to allow the magnesium salts to settle. The supernatant liquid was transferred into another flask, and the residue was extracted with ether (3 × 20 mL). The combined ether extracts were evaporated, and the residue afforded *B*-allenyl-9-BBN after distillation in 75% yield (4.8 g): bp 69 °C/0.5 mm; ^1H NMR ($CDCl_3$) δ 1.2 (br s, 3H), 1.8 (br s, 11H), 4.6 (d, J = 6.3 Hz, 2H), 5.6 (t, J = 12.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.5, 33.3, 33.9, 68.2, 221.1; IR ($CHCl_3$) 1905 cm^{-1}. Anal. Calcd for $C_{11}H_{17}B$: C, 82.5; H, 10.62. Found: C, 82.69; H, 10.82.

General Procedure for the Allenylboration of Aldehydes and Ketones with *B*-Allenyl-9-BBN (11). The allenylboration of propionaldehyde with *B*-allenyl-9-BBN is representative. Propionaldehyde (0.58 g, 10 mmol) was added dropwise at 25 °C to the solution of **11** (1.6 g, 10 mmol) in ether (10 mL). The progress of the reaction was monitored by ^{11}B NMR. As the reaction progresses, the signal at δ 79 ppm, that of *B*-allenyl-9-BBN, changes to δ 52 ppm corresponding to the borinate product. The reaction mixture was stirred for 15 min and then oxidized in the usual manner using 3.3 mL of 3.0 M NaOH and 3.0 mL of 30% hydrogen peroxide. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The resulting colorless liquid was distilled to obtain pure 5-hexyn-3-ol (**14a**) in 82% yield (0.78 g): bp 74−76 °C (60 mm) [lit.[20] bp 73−76 °C (60 mm)]; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3H), 1.5 (m, 2H), 2.0−2.1 (m, 2H), 2.3−2.5 (m, 2H), 3.7 (m, 1H).

2-Methyl-5-hexyn-3-ol (14b): 88% yield; bp 82−84 °C (60 mm) [lit.[20] bp0 78−83 °C (60 mm)]; ^1H NMR ($CDCl_3$) δ 0.9 (m, 6H), 1.8 (m, 1H), 2.1 (t, 1H), 2.3−2.5 (m, 2H), 3.5 (m, 1H).

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2,2-Dimethyl-5-hexyn-3-ol (14c): 89% yield; bp 90–91 °C (70 mm) [lit.[8b] bp 87 °C (66 mm)]; ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9H), 2.0 (t, 1H), 2.1 (br s, 1H), 2.2–2.5 (m, 2H), 3.5 (t, 1H).

1-Phenyl-3-butyn-1-ol (14d): 82% yield; bp 70 °C (2 mm) [lit.[21] bp 89–95 °C (0.6 mm)]; ^{1}H NMR ($CDCl_3$) δ 2.1 (t, 1H), 2.4 (br s, 1H), 2.7 (d, 2H), 4.9 (t, 1H), 7.3–7.4 (m, 5H).

1-(2'-Furfuryl)-3-butyn-1-ol (14e): 79% yield; bp 62 °C (0.6 mm); ^{1}H NMR ($CDCl_3$) δ 2.1 (t, J = 2.6 Hz, 1H), 2.4 (br s, 1H), 2.8 (dd, 2H), 4.9 (t, 1H), 6.4 (s, 2H), 7.4 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.85, 65.88, 70.94, 79.95, 106.51, 110.12, 142.10, 154.59; MS (70 eV, 250 °C) m/z 136 (M^+, 3.22), 119 (M − OH, 13.59), 97 (M − C_3H_3, 100); IR (neat) 3305 (s), 2130 (s), 1611 (m), 1504 (m) cm^{-1}. Anal. Calcd for $C_8H_8O_2$: C, 70.5; H, 5.8. Found: C, 70.23; H, 5.84.

3-Methyl-5-hexyn-3-ol (14f): 89% yield; bp 48 °C (15 mm) [lit.[20] bp 78–79 °C (60–65 mm)]; ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.2 (s, 3H), 1.6 (m, 2H), 1.9 (br s, 1H), 2.1 (t, 1H), 2.4 (d, 2H).

2,2,3-Trimethyl-5-hexyn-3-ol (14g): 88% yield; bp 51 °C (15 mm) [lit.[22] bp 55–60 °C (11 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.0 (s, 9H), 1.3 (s, 3H), 1.8 (br s, 1H), 2.1 (t, 1H), 2.3–2.6 (dd, 2H).

2-Phenyl-4-pentyn-2-ol (14h): 86% yield; bp 74 °C (0.4 mm) [lit.[8b] bp 63 °C (0.05 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.6 (s, 3H), 2.1 (t, J = 5.25 Hz, 1H), 2.4 (br s, 1H), 2.6–2.8 (m, 2H), 7.2–7.5 (m, 5H).

1,1-Diphenyl-3-butyn-1-ol (14i): 90% yield; bp 132 °C (0.5 mm) [lit.[20] bp 125–126 °C (0.3 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.9 (t, 1H), 3.0 (br s, 1H), 3.2 (d, 2H), 7.1–7.5 (m, 10H).

3-Methylhexa-1-en-5-yn-3-ol (14j): 71% yield; bp 86 °C (78 mm); ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 3H), 2.1 (t, 1H), 2.2 (br s, 1H), 2.4 (d, 2H), 5.2–5.4 (m, 2H), 5.9–6.1 (q, 1H); ^{13}C NMR ($CDCl_3$) δ 26.85, 32.85, 71.33, 71.80, 80.24, 112.83, 143.14.

3-Ethyl-5-hexyn-3-ol (14k): 87% yield; bp 80 °C (40 mm) [lit.[8b] bp 60 °C (12 mm)]; ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 6H), 1.7 (br s, 1H), 1.5–1.6 (m, 4H), 2.1 (t, 1H), 2.3 (d, 2H).

1-(2'-Propynyl)-1-cyclohexanol (14l): 88% yield; bp 70 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 1H), 1.4–1.7 (m, 9H), 1.8 (br s, 1H), 2.1 (t, 1H), 2.4 (d, 2H).

1-(2'-Propynyl)-1-cyclopentanol (14m): 87% yield; ^{1}H NMR ($CDCl_3$) δ 1.6–1.8 (m, 6H), 1.8–1.9 (m, 2H), 1.9 (br s, 1H), 2.0 (t, 1H), 2.5 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 23.77, 31.11, 38.82, 70.17, 80.66, 81.40.

Allenylboration of Acid Chlorides and Imines: General Procedure. These reactions were essentially carried out under the same conditions as described above with the reaction stoichiometries adjusted as necessary.

4-Methyl-1,6-heptadiyn-4-ol (20a): 72% yield; bp 66–68 °C (25 mm); ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 3H), 2.1 (t, J = 5.2 Hz, 2H), 2.3 (br s, 1H), 2.5 (t, J = 5.2 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 25.84, 31.37, 70.99, 71.48, 80.17; MS (70 eV, 250 °C) m/z 105 (M − OH, 5), 83 (M − C_3H_3, 20), 43 (CH_3CO^+, 100). Anal. Calcd for $C_8H_{10}O$: C, 78.6; H, 8.19. Found: C, 78.32; H, 7.96.

4-Phenyl-1,6-heptadiyn-4-ol (20b): 76% yield; bp 82–84 °C (0.4 mm); ^{1}H NMR ($CDCl_3$) 2.1 (t, J = 5.3 Hz, 2H), 2.8 (br S, 1H), 2.9 (d, J = 2.7 Hz, 4H), 7.3–7.6 (m, 5H); ^{13}C NMR ($CDCl_3$) 32.02, 72.06, 74.25, 79.65, 125.23, 127.58, 128.16, 143.48; MS (70 eV, 250 °C) m/z 168 (M − OH, 2), 145 (M − C_3H_3, 22), 105 ($C_6H_5CO^+$, 100), 77 (38). Anal. Calcd for $C_{13}H_{12}O$: C, 84.78; H, 6.52. Found: C, 84.83; H, 6.54.

***N*-Benzyl-2-methyl-5-hexynyl-3-amine (22a)**: 90% yield; bp 80 °C/0.2 mm; ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 6H), 1.5 (br s, 1H), 1.9 (m, 1H), 2.0 (t, 1H), 2.2–2.5 (m, 3H), 3.6–3.9 (q, 2H), 7.2–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.63, 20.39, 30.45, 51.48, 60.89, 69.85, 82.17, 126.77, 128.24, 140.70. Anal. Calcd for $C_{14}H_{19}N$: C, 83.58; H, 9.45; N, 6.96. Found: C, 83.62; H, 9.66; N, 7.22.

***N*-Benzyl-1-phenyl-3-butynylamine (22b)**: 84% yield; bp 120–122 °C/0.4 mm; ^{1}H NMR ($CDCl_3$) δ 2.0 (t, J = 5.2 Hz, 1H), 2.1 (br s, 1H), 2.5 (dd, 2H), 3.5–3.7 (q, 2H), 3.8–3.9 (t, 1H), 7.2–7.5 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 28.17, 51.32, 60.64, 70.47, 81.50, 126.86, 127.12, 127.50, 128.04, 128.32, 128.45, 140.22, 142.40. Anal. Calcd for $C_{17}H_{17}N$: C, 86.80; H, 7.23; N, 5.96. Found: C, 86.41; H, 7.29; N, 6.06.

Allenylboration of Esters (Ethyl Acetate). This reaction was carried out as described above up through the addition of the ester. It was necessary to reflux the reaction mixture for 48 h in hexane to afford a decent yield of the product. Analysis of the product indicated the formation of product **20a** (60% overall) along with other impurities (15%).

General Procedure for the Determination of Chemoselectivity of 11 toward Various Carbonyl Compounds. Reaction of benzaldehyde and acetophenone with **11** is representative. To a solution of benzaldehyde (0.53 g, 5 mmol), acetophenone (0.6 g, 5 mmol), and n-undecane (0.39 g, 2.5 mmol), internal standard for GC analysis, in 10 mL of ether at −78 °C was added **11** (0.8 g, 5 mmol) in a dropwise manner. After the mixture was stirred for 4 h at −78 °C, excess acetaldehyde (1 mL) was added to the reaction mixture and slowly warmed to room temperature. The reaction mixture was oxidized in the usual way with NaOH and H_2O_2. The organic layer was separated, dried over anhydrous $MgSO_4$, and analyzed by GC to check the ratio of the products formed (absence of the product from the reaction of acetaldehyde and *B*-allenyl-9-BBN indicated the completion of the reaction in <4 h at −78 °C).

In a separate experiment 5 mmol of allenylmagnesium bromide in ether was added to a solution of benzaldehyde and acetophenone (5 mmol each) in ether at −78 °C and worked up in the usual manner after acetaldehyde was added. The organic layer was dried over anhydrous $MgSO_4$ and was analyzed by GC, and the results from this experiment were compared with those from the previous experiment.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of all new compounds (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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