Transfer of alk-1-enyl group from boron to boron: preparation of *B*-[(*E*)-alk-1-enyl]-9-borabicyclo[3.3.1]nonane

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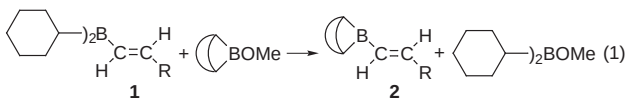
Treatment of (*E*)-alk-1-enyldicyclohexylborane 1 with *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-MeO-9-BBN) at 0 °C results in transfer of alk-1-enyl group from boron to boron to give *B*-[(*E*)-alk-1-enyl]-9-BBN 2 with retention of configuration.

Alkenylboranes have been widely used as one of the most important intermediates in organic synthesis, and generally they are prepared by hydroboration of alkynes with borane derivatives.[1] In some cases, however, hydroboration is not necessarily the most reliable route. For example, a stoichiometric hydroboration of alk-1-yne with 9-BBN is not efficient because it causes dihydroboration to give a significant amount of 1,1-diboryl adduct.[2,3] In order to suppress the dihydroboration, the reaction requires a 100% excess of alk-1-yne and must be carried out at 0 °C for 18 h.[2]

We recently reported that hydroboration of alk-1-ynes with 1,3,2-benzodioxaborole (catecholborane) and hydroboration of 1-haloalk-1-ynes with 9-BBN, both of which are sluggish at room temperature in THF,[4] are accelerated by addition of a catalytic amount (5 mol%) of dicyclohexylborane in THF to afford *B*-[(*E*)-alk-1-enyl]catecholborane and *B*-[(*Z*)-1-haloalk-1-enyl]-9-BBN in high yields, respectively.[5] Dicyclohexylborane probably plays a critical role in a catalytic cycle. In the former reaction, it is presumed that dicyclohexylborane would hydroborate the alk-1-yne and the resulting (*E*)-alk-1-enyldicyclohexylborane would undergo exchange of the alk-1-enyl group for a hydrogen atom of catecholborane to give *B*-[(*E*)-alk-1-enyl]catecholborane with retention of configuration and regeneration dicyclohexylborane. The latter dicyclohexylborane-promoted hydroboration appears to include a similar catalytic cycle. These exchange reactions may belong to the category of not hydroboration but transfer reaction. It seems probable that such transfer reactions provide a method for the preparation of some alkyl- or alkenyl-boranes whose formation is very difficult or inefficient *via* hydroboration. We report here an efficient and stereoselective preparation of *B*-[(*E*)-alk-1-enyl]-9-BBN **2** *via* treatment of (*E*)-alk-1-enyldicyclohexylborane **1** with a slightly excess of *B*-MeO-9-BBN at 0 °C [eqn. (1)].



1 **2** (1)

The reaction of (*E*)-hex-1-enyldicyclohexylborane **1a** in THF with an equimolar amount of *B*-MeO-9-BBN in hexanes was carried out at 0 °C for 1 h, and the reaction mixture, after removal of solvents, was analysed by ^{1}H NMR spectroscopy. In the alkenyl region, the two double triplets at δ 6.20 and 6.73 arising from **1a** decreased considerably while two double triplets appeared at δ 6.23 and 6.83 (*J* 17.3 Hz, *trans* alkenyl protons), indicating that *B*-[(*E*)-hex-1-enyl]-9-BBN **2a**[2,6] had been formed in a stereoselective manner, the ratio of **1a**:**2a** being 20:80. In the same spectrum we also observed two singlets, one at δ 3.76 arising from the methyl protons of unreacted *B*-MeO-9-BBN and the other at δ 3.69 arising from those of dicyclohexylmethoxyborane. These results suggest that the (*E*)-hex-1-enyl group transferred from the boron atom of **1a** to the boron atom of *B*-MeO-9-BBN with complete retention of the stereochemistry. The reaction at 0 °C for 2 h improved the ratio of **1a**:**2a** to 8:92. The reaction with 1.2 equiv. of *B*-MeO-9-BBN under otherwise identical conditions resulted in a slight increase for **2a**; the **1a**:**2a** ratio was 6:94 (entry 1, Table 1). However, no further improvement in the ratio was achieved by increasing the amount of *B*-MeO-9-BBN to 1.5 equiv.

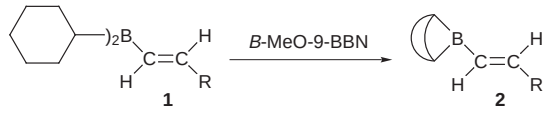
The reaction of various compounds **1** with 1.2 equiv. of *B*-MeO-9-BBN was carried out at 0 °C for 2 h. These results including NMR data for **1** are summarised in Table 1. The reaction of (*E*)-3,3-dimethylbut-1-enyldicyclohexylborane **1b** proceeded smoothly and stereoselectively to give *B*-[(*E*)-3,3-dimethylbut-1-enyl]-9-BBN **2b**; the **1b**:**2b** ratio was 5:95 (entry 2). In the reaction of (*E*)-2-phenylethenyldicyclohexylborane **1c** the reaction mixture was analysed by ^{11}B NMR spectroscopy, since the alkenyl protons of *B*-[(*E*)-2-phenylethenyl]-9-BBN **2c** were indistinguishable from those of **1c**. From the ^{11}B NMR spectrum of the reaction mixture in THF–hexanes‡ **1c** was found to be converted to **2c** with a high ratio (**1c**:**2c** = 1:99) (entry 3). 3-Substituted *B*-[(*E*)-alk-1-enyl]-9-BBN, having a functionality at a position very close to the alkenyl moiety, may be a potential intermediate because of its poly-functional properties. The present transfer reaction is applicable to such functionalised (*E*)-prop-1-enyldicyclohexylboranes without any difficulties. Thus, (*E*)-3-chloroprop-1-enyldicyclohexylborane **1d** and (*E*)-3-methoxyprop-1-enyldicyclohexylborane **1e** were converted to the corresponding compounds **2** stereoselectively (entries 4 and 5). 3-Substituted (*E*)-prop-1-enyldicyclohexylboranes **1f–h** having an oxygen protected with Ac, THP and TMS groups were also converted to *B*-[(*E*)-3-acetoxyprop-1-enyl]-9-BBN **2f**, *B*-[(*E*)-3-(tetrahydro-2*H*-pyran-2-yloxy)prop-1-enyl]-9-BBN **2g** and *B*-[(*E*)-3-(trimethylsiloxy)prop-1-enyl]-9-BBN **2h**, respectively (entries 6–8).

Previously Brown and Gupta reported that boron–carbon bond formation *via* redistribution between trialkylborane and borate required temperatures above 100 °C.[7] It should be noted that the present reaction proceeds smoothly at 0 °C despite the redistribution reaction involving boron–oxygen bond cleavage, and thus appears to be applicable to transfer of alkenyl groups containing a thermally unstable functionality.

One of the characteristic reactions of *B*-alkenyl-9-BBN is the 1,4-addition reaction with but-3-en-2-one.[8] *In situ* addition of **2** to but-3-en-2-one under conditions identical to those described in the literature gave the corresponding 4-(alk-1-enyl)butan-2-one, while the yields were a little lower than those reported. Thus, the present reaction is expected to be synthetically useful, although there may still be room for improvement.

In conclusion, *B*-[(*E*)-alk-1-enyl]-9-BBN **2** can be produced efficiently *via* the reaction of (*E*)-alk-1-enyldicyclohexylborane **1** with *B*-MeO-9-BBN. This transfer of an alk-1-enyl group is performed with complete retention of configuration under very mild conditions. We note that this study provides, to the best of our knowledge, the first example of the transfer of an alk-1-enyl group from boron to boron in stoichiometric amounts. The

Table 1 Reaction of (*E*)-alk-1-enyldicyclohexylborane **1** with *B*-MeO-9-BBN[a]



Entry	R	Alkenyl protons (δ)[b]	Alkenyl protons (δ)[b]	Ratio[c] **1**:**2**
1	Bu^n	**1a** 6.20 (1-H, dt, *J* 17.6 and 1.3 Hz); 6.73 (2-H, dt, *J* 17.6 and 6.5 Hz)	**2a** 6.23 (1-H, dt, *J* 17.3 and 1.3 Hz); 6.83 (2-H, dt, *J* 17.3 and 6.5 Hz)	6:94
2	Bu^t	**1b** 6.11 (1-H, d, *J* 18.1 Hz); 6.88 (2-H, d, *J* 18.1 Hz)	**2b** 6.14 (1-H, d, *J* 17.6 Hz); 6.79 (2-H, d, *J* 17.6 Hz)	5:95
3	Ph	**1c** 7.01 (1-H, d, *J* 18.3 Hz)[d]; [^{11}B NMR δ 72][e]	**2c** 7.00 (1-H, d, *J* 17.8 Hz)[d]; [^{11}B NMR δ 44][e]	1:99[f]
4	CH_2Cl	**1d** 6.45 (1-H, d, *J* 17.6 Hz); 6.56 (2-H, dt, *J* 17.6 and 5.6 Hz)	**2d** 6.49 (1-H, dt, *J* 17.1 and 1.1 Hz); 6.71 (2-H, dt, *J* 17.1 and 5.9 Hz)	7:93
5	CH_2OMe	**1e** 6.42 (1-H, dt, *J* 18.1 and 1.2 Hz); 6.62 (2-H, dt, *J* 18.1 and 4.6 Hz)	**2e** 6.47 (1-H, dt, *J* 17.8 and 1.5 Hz); 6.77 (2-H, dt, *J* 17.8 and 4.5 Hz)	7:93
6	CH_2OAc	**1f** 6.42 (1-H, dt, *J* 18.1 and 1.2 Hz); 6.56 (2-H, dt, *J* 18.1 and 4.6 Hz)	**2f** 6.44 (1-H, dt, *J* 17.6 and 1.5 Hz); 6.71 (2-H, dt, *J* 17.6 and 4.5 Hz)	1:99
7	CH_2OTHP	**1g** 6.44 (1-H, dt, *J* 17.8 and 1.3 Hz); 6.68 (2-H, dt, *J* 17.8 and 4.7 Hz)	**2g** 6.49 (1-H, dt, *J* 17.6 and 1.5 Hz); 6.82 (2-H, dt, *J* 17.6 and 4.4 Hz)	1:99
8	CH_2OTMS	**1h** 6.42 (1-H, dt, *J* 17.8 and 1.6 Hz); 6.68 (2-H, dt, *J* 17.8 and 4.2 Hz)	**2h** 6.47 (1-H, dt, *J* 17.6 and 1.7 Hz); 6.81 (2-H, dt, *J* 17.6 and 4.1 Hz)	5:95

[a] Conditions: **1** (1 equiv.), *B*-MeO-9-BBN (1.2 equiv.), at 0 °C for 2 h. [b] ^{1}H NMR spectra, after removal of solvent(s), were obtained in $CDCl_3$ solutions containing TMS. [c] Determined by ^{1}H NMR spectroscopy. [d] The signal of the other alkenyl proton overlapped that of the phenyl protons. [e] ^{11}B NMR spectra (δ relative to $BF_3{\cdot}OEt_2$) were obtained in THF or THF–hexanes solutions. [f] Determined by ^{11}B NMR spectroscopy.

scope and limitations of this reaction are now under investigation.

Notes and References

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‡ The spectrum exhibited an additional two singlets, one of which was *B*-MeO-9-BBN (δ 56.5) and the other was dicyclohexylmethoxyborane (δ 52). In the ^{11}B NMR analysis using $CDCl_3$ solutions, the signal of **2c** was indistinguishable from that of **1c**.

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