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Carbometalations of Simple Alkenes with Allyldibromoborane

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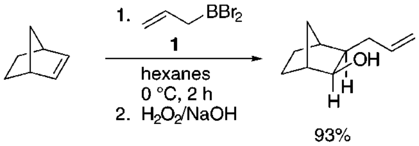
ABSTRACT



The allylboration of alkenes with allyldibromoborane is described. Utilizing an improved methodology for the synthesis of allyldibromoborane, 1,3-dienes, styrene, and even isolated alkenes could be carbometalated in high yield regio- and stereospecifically at 0 °C. This high reactivity of allyldibromoborane significantly expands the scope of carbometalations of alkenes.

The development of methodology for the carbometalation of simple alkenes has been a challenging goal for organic chemists. While general methodologies have been developed for the carbometalation of electron-deficient alkenes (e.g., cuprate chemistry) and isolated alkynes, carbometalations of unactivated alkenes and dienes have been more limited. Useful examples include polymerizations, intramolecular cyclizations,[1] additions to allylic alcohols or amines,[2] and uncatalyzed[3] and catalyzed[4] additions to terminal and highly strained alkenes.[5] Carbometalations with allylic reagents, describable as metallo−ene reactions, have often been more successful. This includes the addition of Grignards and zincs to monosubstituted and strained alkenes,[6] intramolecular examples,[7] and the carbometalations of alkynes and specialized alkenes with allylboranes.[8]

We recently reported on the utility of allylborations with allyldichloroborane.[9] These highly electrophilic reagents rapidly carbometalate allylic silanes and vinyl ethers in high yields. A substantial limitation was that allyldichloroborane was not sufficiently reactive with simple 1,3-dienes, styrenes, and isolated alkenes. At the time we noted that allyldibromoborane (**1**) appeared to be much more reactive and we described in a single example its reaction with 1,3-cyclohexadiene to form an addition product in moderate yield. Unfortunately, our in situ synthesis of **1** was not clean, and the apparent destruction of alkenes by byproducts formed in the process hampered the exploration of **1**'s carbometalation chemistry.

Taking advantage of an improved synthesis of **1**, we report here on its allylboration reactions. It is found that **1** carbometalates simple alkenes and dienes regio- and stereospecifically in high yield.

The NMR observation of **1** from the reaction of BBr_3 with allyltrialkylstannanes had been previously reported,[10] and we have reported the analogous reaction with allyltrimethyl-

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[1] Barluenga, J.; Sanz, R.; Granados, A.; Fañanás, F. J. *J. Am. Chem. Soc.* **1998**, *120*, 4865. Shaughnessy, K. H.; Waymouth, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5873. Negishi, E.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* **1994**, *116*, 8404. Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454.

[2] Richey, H. G., Jr.; Erickson, W. F.; Heyn, A. S. *Tetrahedron Lett.* **1971**, *48*, 2183. Eisch, J. J.; Merkley, J. H.; Galle, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 1148. See also: Hoveyda, A. H.; Xu, Z.; Morken, J. P.; Houri, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 8950.

[3] Lehmkuhl, H. *Bull. Chim. Soc. Fr. II* **1981**, 87.

[4] Dzhemilev, U. M.; Vostrikova, O. S. *J. Organomet. Chem.* **1985**, *285*, 43. Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079. Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266.

[5] Nakamura, E.; Nakamura, M.; Miyachi, Y.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 99.

[6] Lehmkuhl, H. In *Organometallics in Organic Synthesis*; De Meijere, A., Dieck, T., Eds.; Springer-Verlag: New York, 1987; pp 185−202. Nakamura, M.; Arai, M. Nakamura, E. *J. Am. Chem. Soc.* **1995**, *117*, 1179. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.

[7] Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38.

[8] For reviews, see: Mikhailov, B. M. *Russ. Chem. Rev.* **1976**, *45*, 557. Bubnov, Y. N. *Pure Appl. Chem.* **1987**, *59*, 895.

[9] Singleton, D. A.; Waller, S. C.; Zhang, Z.; Frantz, D. E.; Leung, S.-W. *J. Am. Chem. Soc.* **1996**, *118*, 9986−9987.

[10] Harston, P.; Wardell, J. L.; Marton, D.; Tagliavini, G.; Smith, P. J. *Inorg. Chim. Acta* **1989**, *162*, 245.

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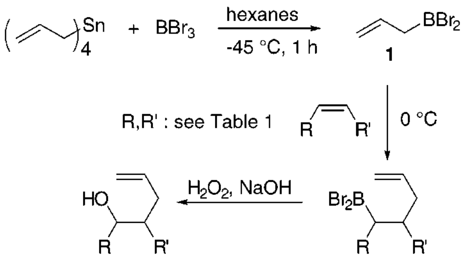
silane.[9] Considerable effort to optimize these reactions failed to provide clean solutions of **1** for alkene allylborations. However, a report by Serre and Guillemin of the synthesis of **1** from tetraallylstannane provided a solution to the problem.[11] In a modification of their procedure, we were able to generate **1** cleanly by the slow addition of 0.27 equiv of tetraallylstannane to a 1.0 M solution of BBr_3 in hexanes (−45 °C, 1 h) (Scheme 1).

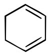
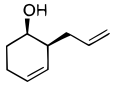
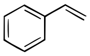
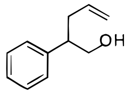
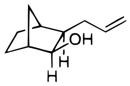
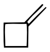
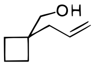
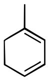
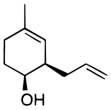
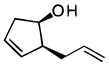
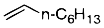
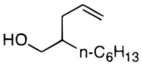
Scheme 1



With an efficient and convenient route to **1** in hand, the carbometalations of a number of alkenes and dienes were investigated. It proved efficient to generate **1** as mentioned above and then add the alkene (0.5 equiv) at −45 °C. The solution was then warmed slowly to 0 °C and allowed to stir for the indicated time. Reactions on an ≈1 mmol scale were worked up by first adding triethylamine (1 mL), followed by 3 N NaOH (3 mL), THF (3 mL), and finally H_2O_2 (1 mL, dropwise). The resulting alcohol products were isolated by flash chromatography.

The results are summarized in Table 1. The additions to 1,3-dienes and styrene are rapid and uniformly regiospecific. In contrast to our previous result, 1,3-cyclohexadiene is carbometalated in high yield. Most striking are the results with isolated alkenes. The clean carbometalation of norbornylene forms only the exo,syn-addition adduct with no rearrangement products. The allylboration of 1-octene is noteworthy as it is completely unactivated and unstrained. Although the yield is lower in this case, this is probably in part due to the allylboration product being comparably reactive to the 1-octene.

Table 1. Allylborations with Allyldibromoborane

substrate	conditions[a]	product	yield[b]
	2 h	 **2**	90%
	2 h	 **3**	83%
	2 h	 **4**	93%
	3 h	 **5**	62%
	2 h	 **6**	56%
	1 h	 **7**	72%
	3 h	 **8**	33%

[a] All reactions were carried out at 0 °C in a hexanes solution for the indicated time. [b] Yields reported are isolated.

The lack of rearrangement products with norbornylene and the general observation of syn addition is consistent with a concerted metallo−ene mechanism. However, the regiochemistry of the additions suggests electrophilic attack by the boron with substantial positive charge buildup within the alkene. Taken as a whole, these results are consistent with the asynchronous but concerted allylboration transition state predicted previously in theoretical calculations.[9]

The combination of the high reactivity of **1** with simple alkenes and dienes and the versatility of the products constitutes a significant extension to alkene carbometalation methodology. We are continuing to investigate these reactions with an emphasis on stereocontrol as well as enhanced reactivity of allylborane derivatives.

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Supporting Information Available: ^1H NMR spectra and tabulated ^{13}C data for new compounds and explanations for stereochemical assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Serre, S. L.; Guillemin, J.-C. *Organometallics* **1997**, *16*, 5844−5848.