

Boron-Activation of Acetylenes to Nucleophilic Addition Reactions

Manning P. Cooke, Jr.*

Department of Chemistry, Washington State University, Pullman, Washington 99164

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Summary: Nucleophilic carbon centers formed through metal-halogen exchange reactions have been found to undergo rapid intramolecular addition reactions with boron-activated acetylenes giving 4- and 5-membered cyclic boron-stabilized vinyl anions which may be trapped with electrophiles. Adducts of these anions with aldehydes fail to undergo the boron-Wittig reaction, but instead undergo acid-catalyzed dehydration to dimesitylboryl-substituted dienes.

The addition of nucleophiles to activated olefins constitutes an important class of carbon-carbon bond-forming reactions.¹ While in principle boron-containing groups should be excellent activators for such addition reactions, owing to boron's great computed ability to stabilize resulting carbanions,² ate-complex formation between the electron-deficient boron atom and the nucleophile normally preempt such addition reactions. We recently reported that certain α -substituted vinylboranes containing sterically demanding mesityl groups are excellent Michael acceptors owing to steric suppression of ate-complex formation.³ Less shielded acetylenic dimesitylborylanes do not undergo intermolecular addition reactions to the triple bond but instead give products which arise from ate-complex formation. Simple vinyl dimesitylborylanes not bearing α -substituents likewise give ate-derived products, but intramolecular metal-halogen exchange-initiated addition reactions are successful.³ We now report successful intramolecular conjugate addition reactions of ω -lithio acetylenic dimesitylborylanes—the first examples of boron-promoted nucleophilic additions to the carbon-carbon triple bond.⁴

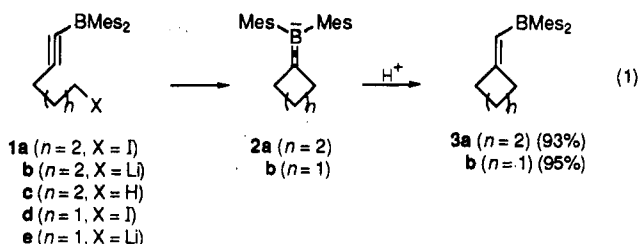
Treatment of **1a**⁵ in Et₂O,⁷ with 2 equiv of *t*-BuLi at -78 \rightarrow 0 $^{\circ}$ C, gave through rapid metal-halogen exchange **1b**

Table 1. Reactions of **2a** with Electrophiles

electrophile	product, E	yield (%)
MeI	4, Me	84
EtI	5, Et	78
BnBr	6, Bn	96
CH ₂ =CHCH ₂ Br	7, CH ₂ CH=CH ₂	86
I ₂	8, I	57
BrCH ₂ COOMe	9, Br	52
MeSSMe	10, SMe	71
Oct-CHO	11, CH(OH)Oct	75 ^a
PhCHO	12, CH(OH)Ph	65 ^a

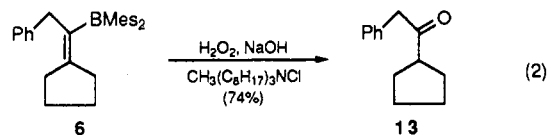
^a Overall yield of diene **16** after dehydration.

which rapidly cyclized to the yellow boron-stabilized anion **2a** (eq 1). Protonation of this anion with MeOH gave



cyclic vinylborane **3a** in 93% yield. No **1c** could be detected when attempts were made to intercept **1b** by quickly quenching reaction mixtures with MeOH at -78 $^{\circ}$ C. Similarly, **1d** was converted into cyclobutylidene derivative **3b** in 95% yield.

Anion **2a** also could be trapped with a variety of electrophiles (Table 1). Alkylation with common halides gave high yields of functionalized vinylboranes **4-7**.⁸ Oxidation of **6** with alkaline H₂O₂ in the presence of a phase-transfer catalyst (Aliquat 336) gave ketone **13** in 74% isolated yield (eq 2).



The reaction of **2a** with I₂ and MeSSMe give the iodide **8** and sulfide **10**, respectively, but the attempted use of methyl bromoacetate as an alkylating agent resulted in the formation of bromovinyl derivative **9**. In general, anion **2a** was found to react only with electrophiles which are able to negotiate the narrow channel leading to the nucleophilic center. Sterically more demanding electro-

(8) The alkylation of structurally similar anions prepared by demetalation reactions of (α -metallovinyl)dimesitylborylanes and the oxidation of resulting vinylboranes to ketones has been reported recently: Pelter, A.; Smith, K.; Parry, D. E.; Jones, K. D. *Aust. J. Chem.* 1992, 45, 57.

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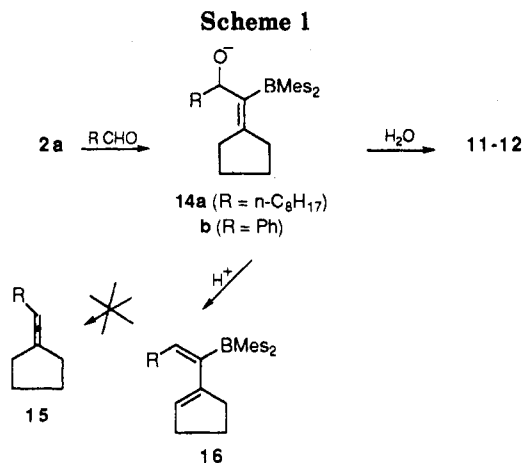
(3) Cooke, M. P., Jr.; Widener, R. K. *J. Am. Chem. Soc.* 1987, 109, 931.

(4) For previous studies on the cyclization reactions of acetylenic alkyllithium intermediates, see: (a) Kandil, S. A.; Deasy, R. E. *J. Am. Chem. Soc.* 1966, 88, 3027. (b) Bailey, W. F.; Ovaska, T. V.; Leipert, T. K. *Tetrahedron Lett.* 1989, 30, 3901. (c) Bailey, W. F. *Ibid.* 1990, 31, 627. (d) Wu, G.; Cederbaum, F. E.; Negishi, E. *Ibid.* 1990, 31, 493. (e) Bailey, W. F.; Ovaska, T. V. *Organometallics* 1990, 9, 1694. (f) Bailey, W. F.; Ovaska, T. V. *J. Am. Chem. Soc.* 1993, 115, 3080. (g) Cooke, M. P., Jr. *J. Org. Chem.* 1993, 58, 6833.

(5) Prepared from Mes₂BF and known⁶ ω -iodo lithioacetylides.

(6) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* 1986, 108, 7791.

(7) Lower yields and less clean reactions resulted when THF was employed.



philes such as Me_3SiCl , Ac_2O , and BzCl did not react with **2a**, while acetone and acetyl chloride served as acids to immediately quench **2a** and give **3a**.

Aldehydes, on the other hand, react rapidly with **2a** giving alcohols **11-12** (Scheme 1). Surprisingly, the adduct alcohols **14** did not undergo the boron-Wittig olefination

reaction⁹ to give **15**, even when heated. Under acidic conditions, alcohols **11-12** rapidly dehydrated giving dienylboranes **16**¹⁰ (Scheme 1). Less highly substituted α -dimesitylborylvinyl alcohols reportedly give allenes under acid conditions.^{9d} In our case, additional substitution results in a more stable intermediate carbocation in the dehydration pathway, and models suggest that the more highly substituted olefin in **11** and **12** causes increased resistance in the formation of the tetrahedral boron atom required in the pathway leading to **15**.

Supplementary Material Available: Experimental procedures and characterization data for **1a**, **1d**, **3-13**, and **16** (9 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.

(9) (a) Pelter, A.; Singaram, B.; Wilson, J. W. *Tetrahedron Lett.*, **1983**, *24*, 635. (b) Pelter, A.; Buss, D.; Colclough, E.; Singaram, B. *Tetrahedron* **1993**, *49*, 7077. (c) Pelter, A.; Buss, D.; Colclough, E.; Singaram, B. *Ibid.* **1993**, *49*, 7077. (d) Pelter, A.; Smith, K.; Jones, K. D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 747.

(10) The *Z*-stereochemistry depicted in **16** follows from stereoelectronic considerations and NOE data; e.g., irradiation of the mesityl *o*-methyl groups in **16a** gave a 20% NOE on the exo-cyclic vinyl hydrogen resonance.