

Preparation of Alcohols from Alkenes via the Homologation of Boronates with (Trimethylsilyl)diazomethane

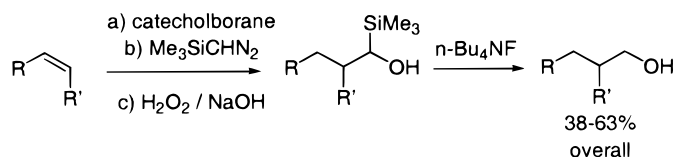
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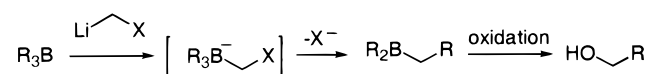
ABSTRACT



Alkylcatecholboranes obtained from alkenes were converted to the corresponding alkylmethanols by reaction with (trimethylsilyl)diazomethane followed by oxidation and treatment with fluoride.

Simple procedures allowing for elongation of the carbon chain of organic molecules are often needed in the course of multistep syntheses. Several methods for the conversion of alkenes to the corresponding alkylmethanols have been described, such as the reaction of boron compounds with carbon monoxide in the presence of a hydride, followed by basic hydrolysis.¹ Other methods involve the reaction of a boron compound with a nucleophilic reagent possessing a leaving group.² The ate complex formed initially can then rearrange to yield a homologated boron compound which can then be oxidized to an alcohol (Scheme 1). To be of

Scheme 1



synthetic utility, it is crucial that only one homologation takes place in the process.

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(1) Brown, H. C.; Hubbard, J. L.; Smith, K. *Synthesis* **1979**, 701.

(2) For reviews, see: (a) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988. (b) Vaultier, M.; Carboni, B. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., McKillop, A., Eds.; Pergamon: Oxford, 1995; Vol. 11, pp 191–276.

Reagents such as dimethylsulfoxonium methylide³ or dimethylsulfonium methylide⁴ lead to mixtures of homologated and polyhomologated products. The preparation of polymers by reaction of boron compounds with diazoalcanes⁵ and dimethylsulfoxonium methylide⁶ has been reported. It is possible to obtain only monohomologated compounds using (chloromethyl)lithium or (bromomethyl)lithium generated in the presence of a boronic ester⁷ or using (dichloromethyl)lithium followed by in situ reduction with potassium triisopropoxyborohydride.⁸ Monohomologation is also obtained when halo(trialkylsilyl)methylolithium is reacted with an organoborane⁹ or a boronate.¹⁰ After removal of the

(3) Tufariello, J. J.; Lee, L. T. C. *J. Am. Chem. Soc.* **1966**, *88*, 4757.

(4) Tufariello, J. J.; Wojtkowski, P.; Lee, L. T. C. *Chem. Commun.* **1967**, 505.

(5) (a) Meerwein, H.; Hinz, G. *Liebigs Ann. Chem.* **1930**, *484*, 1. (b) Bawn, C. E. H.; Ledwith, A. *Prog. Boron Chem.* **1964**, *1*, 345 and references therein.

(6) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049.

(7) (a) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687. (b) Michnick, T. J.; Matteson, D. S. *Synlett* **1991**, 631.

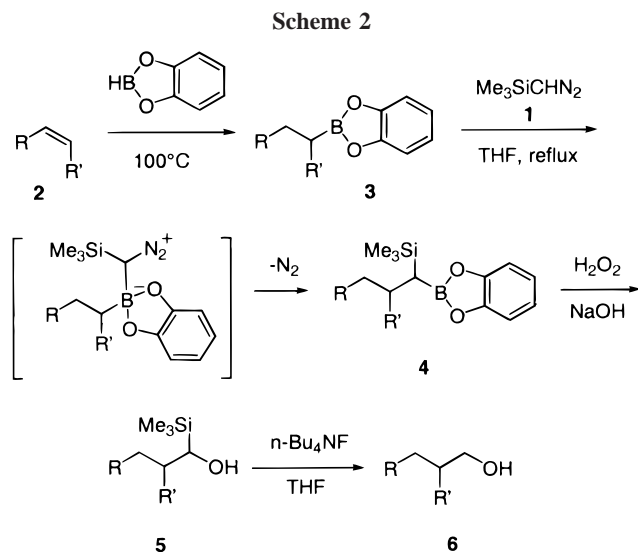
(8) (a) Brown, H. C.; Singh, S. M.; Rangaihenvi, M. V. *J. Org. Chem.* **1986**, *51*, 3150. (b) Brown, H. C.; Singh, S. M. *Organometallics* **1986**, *5*, 994.

(9) Larson, G. L.; Argüelles, R.; Rosario, O.; Sandoval, S. *J. Organomet. Chem.* **1980**, *198*, 15.

(10) (a) Matteson, D. S.; Majumbar, D. *J. Organomet. Chem.* **1980**, *184*, C41. (b) Matteson, D. S.; Majumbar, D. *Organometallics* **1983**, *2*, 230. (c) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.

trialkylsilyl moiety, a homologated boron compound is then obtained, which can be converted to the corresponding alcohol.

In this Letter, we present the conversion of alkenes to the corresponding alkylmethanols using as the key step the reaction of boronates with (trimethylsilyl)diazomethane (**1**),^{11,12} a reagent that is commercially available (Scheme 2).



Thus, alkenes **2** were treated with catecholborane at 100 °C. This hydroboration is known to place selectively the boron atom on the less hindered carbon atom of the alkene and to yield mainly the *exo* isomer from norbornene.¹³ After removal of excess catecholborane, the boronates **3** obtained were diluted in THF and heated in the presence of 3–5 equiv of **1** for 10 h. Oxidation by alkaline H₂O₂ then afforded α -(trimethylsilyl)alcohols **5**, which were purified by chromatography. Compound **5e** was obtained as a mixture of diastereomers.


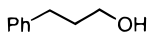
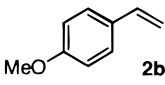
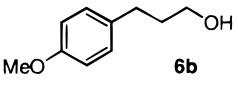

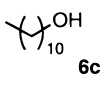

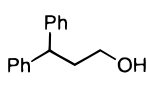

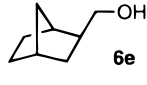
Alcohols **6** were then obtained after treatment with tetrabutylammonium fluoride, with an overall yield of 38–63% from alkenes **2**, as summarized in Table 1. A reaction was also carried out using the recrystallized boronate prepared from catecholborane and 4-vinylanisole. It reacted with **1** under the conditions described above to afford, after oxidation, silanol **5b** in 63% yield and the nonhomologated alcohol 2-(4-methoxyphenyl)ethanol in 27% yield. This indicates that the reaction of the boronate with **1** is the step determining the overall yield of the process, rather than the hydroboration or the desilylation.

(11) For reviews, see: (a) Shioiri, T.; Aoyama, T. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley and Sons: Chichester, 1995; Vol. 7, pp 5248–5251. (b) Anderson, R.; Anderson, S. B. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; Jai Press: London, 1991; Vol. 1, pp 303–325.

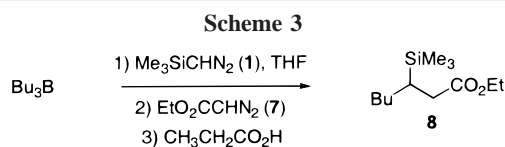
(12) The preparation of 10-trimethylsilyl-9-borabicyclo[3.3.2]decane by reaction of (trimethylsilyl)diazomethane with *B*-methoxy-9-BBN followed by reduction has been reported: Soderquist, J. A.; Matos, K.; Vaquer, J.; Huang, S. D. *Book of Abstracts*, 214th National Meeting of the American Chemical Society, Las Vegas, NV, September 7–11, 1997; American Chemical Society: Washington, DC, 1997; ORGN-055.

(13) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249.

Table 1. Alcohols **6** from Alkenes **2**

Alkene 2	Alcohol 6	% Yield (6 from 2)
 2a	 6a	60
 2b	 6b	63
 2c	 6c	38
 2d	 6d	55
 2e	 6e	41

(Trimethylsilyl)diazomethane thus allows one to obtain monohomologated boron compounds. Sequential treatments of boron compounds with monohomologating agents could in principle be employed to prepare diversely functionalized products. To test this possibility, tributylborane in THF was treated with excess **1** (3.6 equiv) for 24 h at room temperature; then excess ethyl diazoacetate (**7**; 3.6 equiv) was added and the solution was refluxed for 12 h (Scheme 3). After



treatment with propionic acid, ethyl 3-(trimethylsilyl)heptanoate (**8**), resulting from two consecutive homologations, was obtained in 33% yield (based on the butyl groups in Bu₃B). Reactions starting from boron compounds having only one transferable group will soon be evaluated.

In conclusion, we have described a practical procedure for the preparation of alkylmethanols from alkenes which makes use of the homologation of alkylcatecholboranes with (trimethylsilyl)diazomethane. The method has the advantage that no generation of lithiated species is needed, and also it avoids the use of toxic carbon monoxide.

Supporting Information Available: Experimental procedures and characterization data for compounds **5a–e**, **6a–e**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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