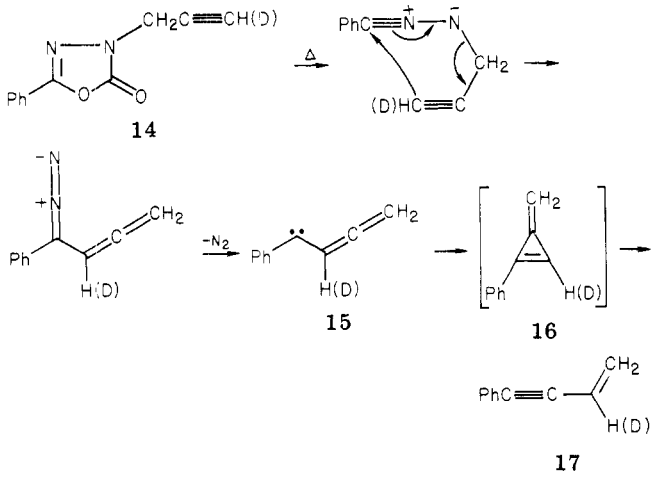

14 15 16 17

of carbon dioxide followed by a 3,3-sigmatropic shift and extrusion of nitrogen would lead to allenylcarbene **15**. Cyclization of this species to methylenecyclopropene **16** followed by ring opening nicely accounts for the formation of **17**. In order to test this postulated mechanism, the corresponding deuterated propargylic compound was prepared and pyrolyzed under identical reaction conditions. If the mechanism depicted above is operative, deuterium should be found only at the C-3 position. This was borne out by experimentation; the final product obtained from the pyrolysis was fully deuterated at C-3.

In summary, all the oxadiazolinones investigated gave products which were consistent with a 3,3-sigmatropic shift of an *N*-allyl-substituted nitrile imine to a *C*-allyl-substituted diazoalkene. A mechanism involving loss of nitrogen and generation of a carbene intermediate provides a common rationalization for the diversity of products formed.

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Registry No. 1, 55084-88-3; 2, 6249-80-5; 3, 2288-18-8; (*E*)-4, 16939-57-4; (*Z*)-4, 31915-94-3; 5, 447-53-0; 6, 74752-47-9; (*E*)-7, 70178-90-4; (*Z*)-7, 64035-02-5; 8, 2717-44-4; 9, 74752-48-0; 10, 74752-49-1; 11, 74752-50-4; 12, 74752-51-5; 13, 74752-52-6; 14, 74752-53-7; 15, 74752-54-8; 16, 74752-55-9; 17, 13633-26-6.

Albert Padwa,* Thomas Caruso, Steven Nahm
Department of Chemistry, Emory University
Atlanta, Georgia 30322
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Homologation of Organoboranes via Carbonylation-Reduction

Summary: Reduction by lithium aluminum hydride of the intermediate formed in the hydride-induced carbonylation of *B*-R-9-BBN provides a valuable new method for the stereospecific homologation of *B*-R-9-BBN → *B*-RCH_2-9-BBN (R = alkyl, cycloalkyl, bicycloalkyl). Since these derivatives are versatile intermediates for organic synthesis, readily transformed into a variety of products, this development makes available a valuable new route to homologated derivatives.

Sir: The utility of boranes in organic synthesis stems in large part from the high regio- and stereoselectivity of their transformations. Application of this chemistry hinges on the availability of regio- and stereochemically pure organoboranes, which in turn is limited by the selectivity of the hydroboration reaction and/or by the availability of the requisite olefin (or alkyne).

Table I. Homologation of *B*-R-9-BBN via Carbonylation-Reduction

R of *B*-R-9-BBN[a]	*B*-RCH_2-9-BBN	yield,[b] %	δ[c]
n-octyl	2	70	81.7
cyclohexyl	4	85	88.2
cyclopentyl	6	65	88.8
cyclooctyl	8	75	84.5
exo-2-norbornyl	12	77	87.3
trans-2-methylcyclopentyl	15	88	87.5

[a] *B*-R-9-BBN was made in situ from 9-BBN and a small excess of the alkene. [b] Distilled yields based on 9-BBN. [c] ^{11}B NMR chemical shifts are relative to $BF_3 \cdot OEt_2$ (δ 0) with chemical shifts downfield assigned as positive.

As part of an ongoing interest in the synthesis of boranes not available via hydroboration,[1] we desired a convenient method for the homologation of organoboranes. Because of the demonstrated usefulness of 9-BBN and its derivatives, a general synthesis of *B*-(alkylmethyl)-9-BBN compounds would be of especial interest. Previous results[2] from a study of the hydride-induced carbonylation of organoboranes[3] suggested that hydride reduction of the intermediate (which provides aldehydes and methylol derivatives upon oxidation and hydrolysis, respectively) might provide a convenient route to these derivatives.

Indeed, we have found that carbonylation of *B*-alkyl-9-BBN, followed by reduction of the intermediate, provides a high-yield, stereospecific synthesis of the homologous borane. Strict temperature control during both steps is crucial for success. Thus, carbonylation[4] at −20 °C in the presence of 1.3 equiv of freshly prepared lithium trimethoxyaluminum hydride (LTMA), reduction at the same temperature[5] with 1.0 molar equiv of lithium aluminum hydride,[6] and hydrolysis of the borohydride formed[7] provides the product in 70–90% distilled yields. The purity is quite high, 97–100% by GLC.[8]

Difficulties were encountered initially in isolating the product from the gelatinous aluminum byproducts until it was found that addition of methanesulfonic acid provides a fine granular precipitate which is easily centrifuged from the reaction mixture, leaving a clear supernatant. This is decanted, concentrated, and distilled to give the product. Table I shows the scope of the process.

For instance, straight-chain alkyl groups can be lengthened by one carbon atom, as shown below for *B*-*n*-octyl-9-BBN (**1**, formed in situ via hydroboration of the readily available 1-octene).

The sequence is also effective for cyclic olefins as substrates, yielding the *B*-cycloalkylmethyl derivatives in good yield.

(1) (a) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1. (b) Brown, H. C.; Sinclair, J. A. *Ibid.* **1977**, *131*, 163. (c) Molander, G. A. Ph.D. Thesis, Purdue University, 1979.

(2) Coleman, R. A.; Hubbard, J. L., unpublished results.

(3) (a) Brown, H. C.; Coleman, R. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 499. (b) Brown, H. C.; Knights, E. F.; Coleman, R. A. *Ibid.* **1969**, *91*, 2144. (c) Brown, H. C.; Hubbard, J. L.; Smith, K. *Synthesis* **1979**, 701.

(4) All carbonylations were performed in an automatic gasimeter available from Ace Glass Inc.

(5) Lack of temperature control at this stage causes loss of product due to dealkylation (exchange with AlH_3).

(6) Two equivalents of $Li(MeO)_3AlH$ is also effective; this provides for 2-carbon homologation of olefins to primary aldehydes via a second carbonylation, followed by oxidation.

(7) Brown, H. C.; Hubbard, J. L.; Singaram, B. *J. Org. Chem.* **1979**, *44*, 5004.

(8) The products were characterized via oxidation to the corresponding methylol derivatives, which were available from the previous study.[3c]

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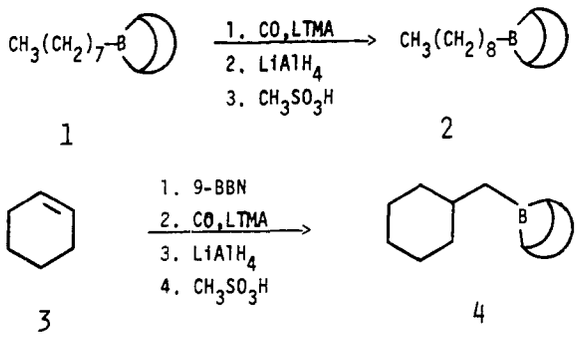
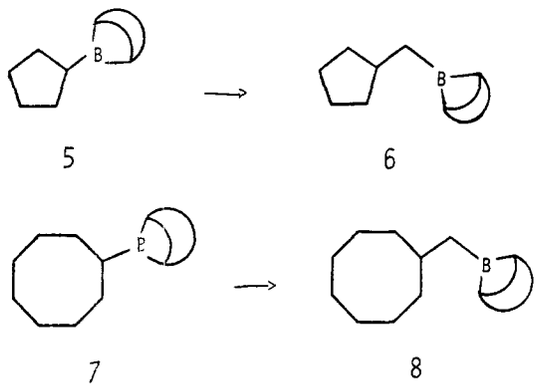
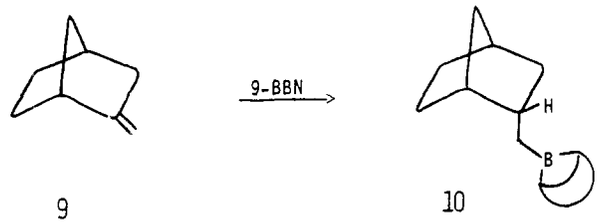


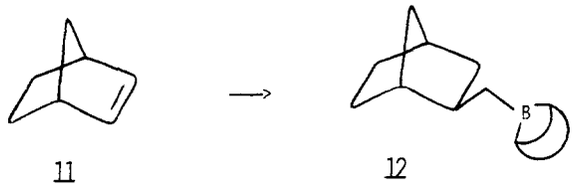
The effect of ring size is negligible (except for effect on the rate of hydroboration). Thus, the cyclopentylmethyl and cyclooctylmethyl derivatives are readily obtained by the process.



The sequence is particularly attractive for those cases where stereoisomers are possible. The stereochemistry is determined by the hydroboration step, since carbonylation has been shown[3b] to proceed with retention of configuration. Thus, although hydroboration of 2-methylenenorbornane (**9**) would be expected to proceed predominantly

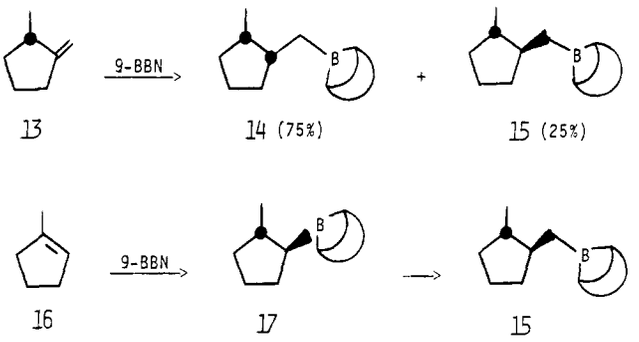


from the exo face to give the endo derivative (**10**), application of our method to norbornene (**11**) provides the exo[9] derivative (**12**).



An equally interesting result was obtained with trisubstituted (cyclic) olefins. Thus, whereas hydroboration of 2-methylmethylenecyclopentane yields a mixture predominating in the cis isomer (**14**), only the trans isomer (**15**) is produced when our process is applied to 1-methylcyclopentene.

The following procedure is representative of the process. A Brown Automatic Gasimeter[4] is oven-dried and set up



for carbonylation under a flow of dry nitrogen as previously described.[10] The reaction flask is charged with 5 mmol of 9-BBN[11] (0.5 M in THF), followed by the alkene. When the hydroboration is complete,[12] 1.3 equiv of $Li(MeO)_3AlH$ (freshly prepared via dropwise addition of 5 M CH_3OH in THF to a standard solution of $LiAlH_4$ in THF[10] at 0 °C) is added rapidly with stirring at −20 °C. A thick gel forms, and the stirrer is stopped as the system is flushed with carbon monoxide via injection of 2 mL of anhydrous formic acid. After the system is at equilibrium, vigorous stirring is begun (removal of the cooling bath may be necessary to initiate stirring due to gel formation; it is then replaced). When absorption ceases (ca. 15 min), the system if flushed with N_2 as the reaction flask is disconnected from the generator system. One mole of $LiAlH_4$ in THF is then added dropwise over 5 min at −20 °C. After 15 min, the cooling bath is removed and the clear, colorless mixture is stirred an additional 45 min at 25 °C. The mixture is then transferred via a double-ended needle to a centrifuge tube[13] (dry, N_2 flushed). Cautious addition (with vigorous stirring) of 0.1 mL of water, followed by 0.75 mL of methanesulfonic acid (Teflon needle) and, finally, 0.9 mL of water yields a flocculent precipitate and a clear upper layer. Centrifugation facilitates the separation. The solid is washed (vigorous shaking, followed by centrifugation) three to five times with THF (5 mL), each extract being monitored for product by GLC. Evaporation of the solvent yields a pale yellow oil, which is bulb-to-bulb distilled to give the homologated organoborane.

Registry No. **1**, 30089-00-0; **2**, 74763-87-4; **3**, 110-83-8; **4**, 74763-88-5; **5**, 49623-12-3; **6**, 74763-89-6; **7**, 67753-92-8; **8**, 74763-90-9; **9**, 497-35-8; **10**, 74763-91-0; **11**, 498-66-8; **12**, 74763-92-1; **13**, 41158-41-2; **14**, 74763-93-2; **15**, 74763-94-3; **16**, 693-89-0; **17**, 63942-79-0; *B*-cyclohexyl-9-BBN, 53535-83-4; *B*-*exo*-2-norbornyl-9-BBN, 67753-91-7; 1-octene, 111-66-0; cyclopentene, 142-29-0; cyclooctene, 931-88-4; $Li(MeO)_3AlH$, 12076-93-6; 9-BBN, 280-64-8.

(9) Liotta, R. Ph.D. Thesis, Purdue University, 1976.

(10) Brown, H. C. "Organic Synthesis via Boranes"; Wiley-Interscience: New York, 1975.

(11) Aldrich Chemical Co.

(12) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.

(13) For a 30-mmol scale or less. For larger scale work, we recommend an alternate procedure. This involves addition of a 1:1 mixture of phosphate buffer (pH 7) and saturated aqueous sodium potassium tartrate (6 mL/mmol). The clear upper layer is separated, dried azeotropically, and distilled to give the product.

(14) Postdoctoral research assistant on Grant CHE 76-20846 provided by the National Science Foundation.

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Herbert C. Brown,* Thomas M. Ford[14]
John L. Hubbard[15]
Richard B. Wetherill Laboratory
Purdue University
West Lafayette, Indiana 47907
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