## Synthesis of B-Cyclopropyl- and B-Cyclobutylbicyclo[3.3.1]nonane via Ring Closure of Boron Intermediates.
A Convenient Entry into Cyclopropyl and Cyclobutyl Derivatives via Hydroboration

Sir:

We wish to report the first successful cyclization of an open-chain boron intermediate to produce a cyclobutylboron moiety. This makes possible a new entry into the cyclobutane system and makes readily available to that system the versatile synthetic possibilities offered by organoboranes.[1]

The reaction involves the dihydroboration of the tosylate of 3-butyn-1-ol with 9-borabicyclo[3.3.1]nonane[2] (9-BBN) (eq 1) followed by treatment with methyllithium (eq. 2).

$$HC\equiv CCH_2CH_2OTs \xrightarrow{9\text{-BBN}} HCCH_2CH_2CH_2OTs \qquad (1)$$

$$\xrightarrow{CH_3Li} \qquad (2)$$
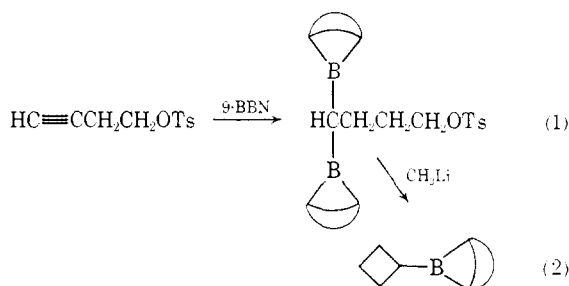
It is now well established that the hydroboration of various allyl derivatives, followed by treatment with appropriate bases, provides a highly convenient entry into the corresponding cyclopropane derivatives (eq 3).[3–6]
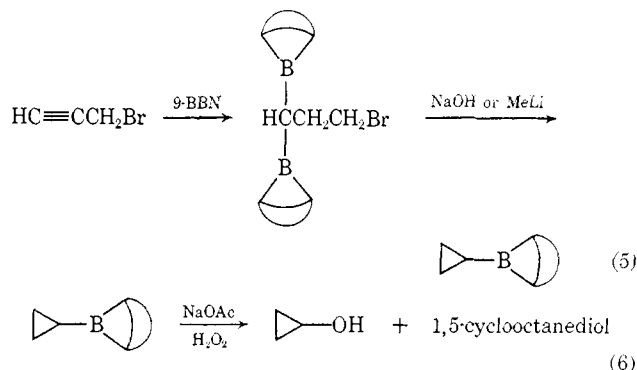
$$CH_2=CHCH_2X \xrightarrow{>BH} CH_2CH_2CH_2 \xrightarrow{base} \triangle \qquad (3)$$
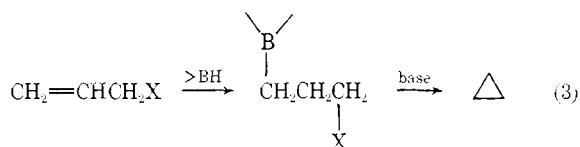
However, all previous attempts to extend this synthesis to the next higher homolog have been unsuccessful.[4,5]

9-BBN possesses major advantages for the cyclopropane synthesis.[6] Moreover, B-alkyl-9-BBN derivatives possess major advantages for many of the new reactions involving organoboranes.[1,7] Consequently, we undertook to explore the synthesis of B-cyclopropyl- and B-cyclobutyl-9-BBN via cyclization reactions.

The synthesis of diethylcyclopropylborane was achieved previouly by Binger and Köster via the dihydroboration of propargyl chloride with diethylborane[8] (cq 4). This same synthesis proceeded satisfactorily with 9-BBN. However, whereas Binger and Köster reported that no simple reaction products could
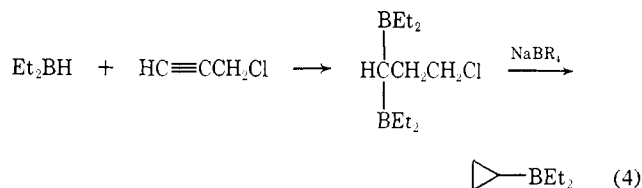
be realized in an attempted cyclization with aqueous sodium hydroxide, we realized a 70% yield of B-cyclopropyl-9-BBN in closure with this reagent (eq 5). Alternatively, methyllithium could be utilized (eq 5). The intermediate is readily oxidized to cyclopropanol with alkaline hydrogen peroxide. Consequently, this provides a convenient new route to cyclopropanol (eq 6).

$$Et_2BH + HC\equiv CCH_2Cl \longrightarrow HCCH_2CH_2Cl \xrightarrow{NaBR_4}$$

$$\triangleright\!\!-BEt_2 \qquad (4)$$

$$HC\equiv CCH_2Br \xrightarrow{9\text{-BBN}} HCCH_2CH_2Br \xrightarrow{NaOH \ or \ MeLi}$$

$$\triangleright\!\!-B \qquad (5)$$

$$\triangleright\!\!-B \xrightarrow[H_2O_2]{NaOAc} \triangleright\!\!-OH + 1,5\text{-cyclooctanediol} \qquad (6)$$

The usual reaction flask was charged with 200 mmol of 9-BBN in THF, and 100 mmol of propargyl bromide was added with cooling. The reaction mixture was allowed to stir for 3 hr at 25°. Then 125 mmol of sodium hydroxide was added as a 3 M aqueous solution and the mixture was stirred for 2 hr. The aqueous phase was saturated with potassium carbonate and the THF layer removed and dried over anhydrous magnesium sulfate. Distillation yielded 11.5 g (70% yield) of B-cyclopropyl-9-borabicyclo[3.3.1]nonane, bp 104° (14 mm). (All operations were carried out under nitrogen.) The pmr spectrum exhibited cyclopropyl protons: 1 H at 0.60 ppm and 4 H at 0.55 ppm. Oxidation of a sample yielded cyclopropanol, bp 100–103°, and *cis*-cyclooctane-1,5-diol, mp 72–73°.

Synthesis of cyclopropanol, without isolation of the intermediate, is described in the following procedure. After treatment with aqueous sodium hydroxide to achieve the closure, as described above, the solution was cooled to 0° and 150 ml of 5 M aqueous sodium acetate was added, followed by the careful addition of 60 ml of 30% hydrogen peroxide. After 1.5 hr, sodium chloride was added to separate the aqueous phase. The THF layer and extracts were dried over anhydrous magnesium sulfate and distilled through a spinning-band column. There was obtained 3.8 g (65% yield) of cyclopropanol, bp 100–103°, with the pmr spectrum exhibiting cyclopropyl protons: 1 H at 2.7 ppm and 4 H at 0.55 ppm (multiplets).

In the case of the cyclobutyl derivative, we decided to use the tosylate as possibly providing maximum driving force for ring closure. Treatment of the dihydroborated intermediate with aqueous sodium hydroxide failed to achieve closure.[9] However, closure was successful with methyllithium.

(1) See H. C. Brown, *Accounts Chem. Res.*, 2, 65 (1969), footnote 5, for a summary of literature references.
(2) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, 90, 5280, 5281, 5283 (1968).
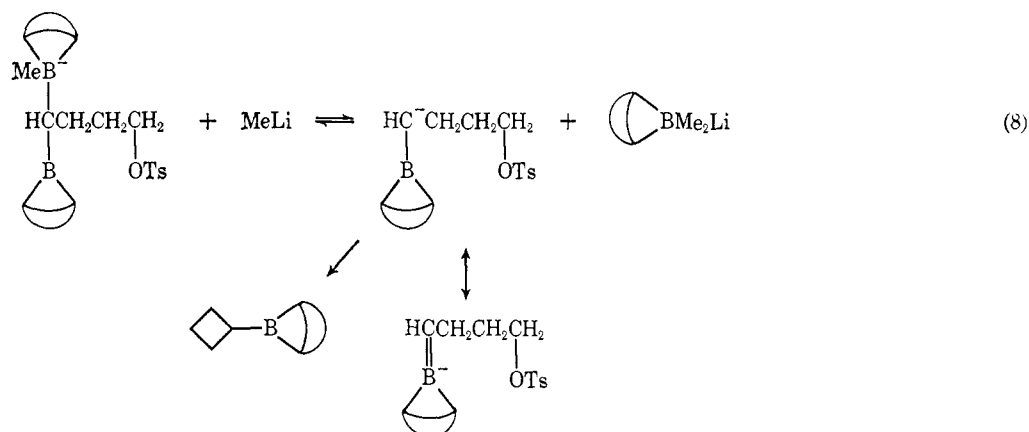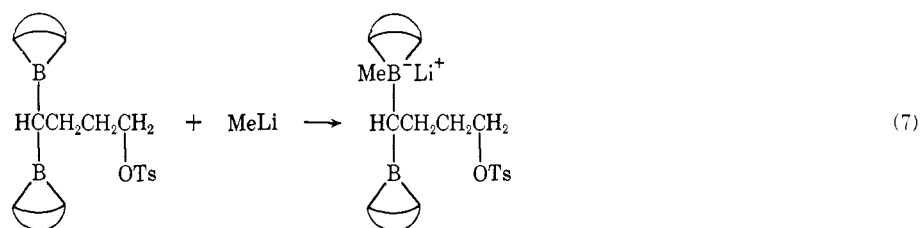(3) M. F. Hawthorne, *ibid.*, 82, 1886 (1960).
(4) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).
(5) H. C. Brown and K. A. Keblys, *J. Am. Chem. Soc.*, 86, 1791 (1964).
(6) H. C. Brown and S. P. Rhodes, *ibid.*, 91, 2149 (1969).
(7) H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, 91, 2144 (1969); H. C. Brown and M. M. Rogić, *ibid.*, 91, 2146 (1969); H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, 91, 2147 (1969).
(8) P. Binger and R. Köster, *Angew. Chem.*, 74, 652 (1962).
(9) Such dihydroborated intermediates undergo rapid hydrolysis: G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.*, 89, 291 (1967).

$$\underset{\text{B}}{\overset{\text{B}}{\mid}}\text{HCCH}_2\text{CH}_2\text{CH}_2 \ + \ \text{MeLi} \ \longrightarrow \ \underset{\text{B}}{\overset{\text{MeB}^-\text{Li}^+}{\mid}}\text{HCCH}_2\text{CH}_2\text{CH}_2 \qquad (7)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{OTs} \qquad\qquad\qquad\qquad \text{OTs}$$

$$\underset{\text{B}}{\overset{\text{MeB}^-}{\mid}}\text{HCCH}_2\text{CH}_2\text{CH}_2 \ + \ \text{MeLi} \ \rightleftharpoons \ \underset{\text{B}}{\overset{\mid}{}}\text{HC}^-\text{CH}_2\text{CH}_2\text{CH}_2 \ + \ \text{BMe}_2\text{Li} \qquad (8)$$
$$\qquad\qquad\qquad \text{OTs} \qquad\qquad\qquad\qquad\qquad \text{OTs}$$

$$\square\text{—B} \qquad\qquad \underset{\text{B}^-}{\overset{\|}{}}\text{HCCH}_2\text{CH}_2\text{CH}_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \text{OTs}$$

3-Butyn-1-ol was converted into the tosylate, $n^{20}\text{D}$ 1.5335, in 80% yield by the usual pyridine procedure. The tosylate, 100 mmol, was hydroborated in the usual manner with 200 mmol of 9-BBN and the solution was allowed to stir for 3 hr at 25°. Then 200 mmol of 1.7 M methyllithium in ethyl ether was added dropwise over 30 min and the solution was allowed to stir for 6 hr. Water, 25 ml, was added, the solution was treated with potassium carbonate, and the organic phase was separated, dried over magnesium sulfate, and distilled. There was obtained 12.6 g (65% yield) of B-cyclobutyl-9-borabicyclo[3.3.1]nonane, bp 113° (10 mm), and 10.2 g (60% yield) of B-methyl-9-BBN, bp 57° (10 mm). (All operations were carried out under nitrogen.) Oxidation of a sample of the B-cyclobutyl-9-BBN yielded cis-cyclooctane-1,5-diol, mp 72–73°, and cyclobutanol, bp 123–125°, $n^{20}\text{D}$ 1.4337, pmr spectrum identical with the published spectrum.[10]

For the synthesis of cyclobutanol, the oxidation of the intermediate was carried out in situ, without isolation, utilizing aqueous sodium hydroxide, 66 ml of 3 M, and 30% hydrogen peroxide, 66 ml. Distillation yielded 4.7 g (65% yield) of cyclobutanol, bp 120–123°, $n^{20}\text{D}$ 1.4305, pmr spectrum identical with that published.[10]

At the present time we are unable to account for the very great difference in the case of closure of the simple hydroboration products of 3-butenyl chloride[4] and tosylate[5] and the present dihydroborated intermediate. Possibly, in the present case, the dissociation of the initial addition compound (eq 7) into the carbanion[11] (eq 8) is greatly stabilized by the possibility of resonance with the second 9-BBN moiety, so that the relatively unfavorable displacement involved in the formation of a four-membered ring can occur.

This opens up the door to a major new route to substituted cyclopropyl- and cyclobutylboron intermedi-

ates and to the numerous derivatives into which such boron compounds can be converted.

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The Heat of Formation of the Methoxycarbonyl Ion

Sir:

The stabilization energy of cations has been the subject of a number of previous investigations.[1-4] Of particular interest is the substituted methyl cation,[4] CH_2X^+, in which the substituents caused very large changes in the stabilization energy of the cation. These changes appear to be due to π-bond interactions between the substituent and the vacant 2p orbital on the carbon bearing the formal charge.[4] As might be expected, the stabilization energy (SE) for X = OCH_3, relative to the CH_3^+ ion as zero, is greater than the SE value for X = CH_3 due to the formation of stable ionic structures such as $\text{CH}_3\text{O}^+\!\!=\!\!\text{CH}_2$.

The stabilization energies of the substituted cations XCO^+ appear to be markedly different from the methyl cations. Recent X-ray data and molecular orbital calculations on the acetyl ion[5] indicate a shortened C–C bond and net positive charge on the carbonyl carbon. Thus both $\text{CH}_3\text{C}^+\!\!=\!\!\text{O}$ and $\text{CH}_3\text{C}\!\!\equiv\!\!\text{O}^+$ are likely representations of the acetyl ion. If a similar net positive charge resides on the carbonyl carbon of the methoxycarbonyl ion then unshared pair donor substituents should cause a marked stabilization of the XCO^+ ion.

(10) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 16, 171 (1960).
(11) Compare G. Zweifel and H. Arzoumanian, *Tetrahedron Letters*, 2535 (1966), and G. Cainelli, G. D. Bello, and G. Zubiani, *ibid.*, 4315 (1966).

(1) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, 50, 901 (1954).
(2) J. Halpern, *J. Chem. Phys.*, 20, 744 (1952).
(3) A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, 82, 1052 (1960).
(4) R. W. Taft, R. H. Martin, and F. W. Lampe, *ibid.*, 87, 2490 (1965).
(5) F. P. Boer, *ibid.*, 88, 1572 (1966).