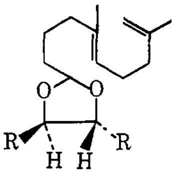

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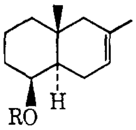

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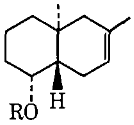

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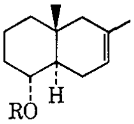

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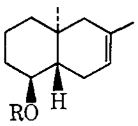

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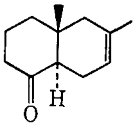

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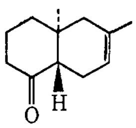

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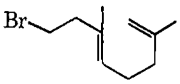

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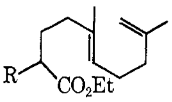

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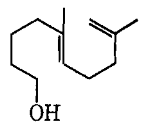

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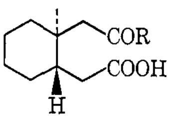

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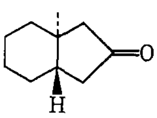

9

formed, upon pyrolysis with lead carbonate,[13] into the hydrindanone **9**,[11] ORD[9b] $[\Phi]_{589}$ +396°, $[\Phi]_{325}$ +10,208°, $[\Phi]_{313}$ +8824°, $[\Phi]_{303}$ +1464°, $[\Phi]_{295}$ −4987°, $[\Phi]_{286}$ −7755°, $[\Phi]_{279}$ −8111° (*c* 0.175, dioxane). The absolute configuration of the pure (+) enantiomer is known to be that shown by formula **9**.[14] In our hands this pure material showed ORD $[\Phi]_{589}$ +450°, $[\Phi]_{32}$ +12,350°, $[\Phi]_{314}$ +10,700°, $[\Phi]_{303}$ +1920°, $[\Phi]_{296}$ −5910°, $[\Phi]_{286}$ −9350°, $[\Phi]_{278}$ −9700° (*c* 0.270, dioxane). Thus the specimen of hydrindanone produced from the octalin contained 92% **9** and 8% of its enantiomer which, in turn, represented the composition of the octalones **4b** and **4a**, respectively. The enantiomeric ratios of various octalone specimens thus were calculated from their ORD curves using the established value, $[\Phi]_{222}$ +11,150°, for the pure enantiomer **4b**.

The asymmetric induction observed in this work affords a clue to the geometry of the transition states for the two cyclization reactions to give products with axial and equatorial side chains. This matter will be considered in a detailed paper. It is noteworthy that application of the method disclosed here to the cyclization of a tetraenic acetal[15] should give optically active tetracyclic products.

Acknowledgment. We wish to express our thanks to Miss Ruth L. Records for performing the ORD measurements and to Professor Carl Djerassi for providing a specimen of the hydrindanone **9**. We also thank the U. S. Public Health Service, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[13] *Cf.* W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg, and L. J. Chinn, *J. Am. Chem. Soc.*, **74,** 2832 (1952).

[14] F. Gautschi, O. Jeger, V. Prelog, and R. B. Woodward, *Helv. Chim. Acta*, **38,** 296 (1955); C. Djerassi and J. E. Gurst, *J. Am. Chem. Soc.*, **86,** 1755 (1964).

[15] *Cf.* W. S. Johnson, K. Wiedhaup, S. F. Brady, and G. L. Olson, *ibid.*, **90,** 5277 (1968).

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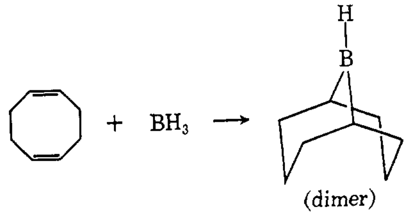
Cyclic Hydroboration of 1,5-Cyclooctadiene. A Simple Synthesis of 9-Borabicyclo[3.3.1]nonane, an Unusually Stable Dialkylborane

Sir:

We wish to report that the reaction of 1,5-cyclooctadiene with borane in tetrahydrofuran can be controlled to provide a convenient synthesis of 9-borabicyclo[3.3.1]nonane (9-BBN, eq 1). This crystalline



(1)

borane, mp 140–142°, possesses remarkable thermal stability.[1] Moreover, it exhibits unusual stability to air oxidation. Yet it hydroborates olefins and acetylenes rapidly and quantitatively.[2] Consequently it promises to become an exceedingly valuable reagent to facilitate syntheses *via* hydroboration.[3]

1,5-Cyclooctadiene has been hydroborated previously.[4] The reaction proceeds rapidly to the dihydroborated species. Since the diols produced upon oxidation of the organoborane species are exclusively *cis*,[4c,d] it is evident that hydroboration must proceed in a rapid transannular manner to form a boron bridge across the ring.

Hydroboration of 1,5-cyclooctadiene with an equimolar amount of borane–tetrahydrofuran (THF) followed by oxidation in alkaline hydrogen peroxide yields 72% *cis*-1,5- and 28% *cis*-1,4-cyclooctanediol.[5]

Distillation of the organoborane intermediate under vacuum (bp 195° (12 mm)) yielded a white solid (mp 140–142°) which underwent oxidation to yield essentially pure (99%) *cis*-1,5-cyclooctanediol (mp 73.5–74.3°, bis-*p*-nitrobenzoate mp 180.3–181.5°).[6] Evidently an isomerization of the 1,4 isomer to the 1,5 had taken place during the distillation.

Actually, the isomerization takes place under exceedingly mild conditions, refluxing for 1 hr at 65° in THF.[7] Since the isomerization of organoboranes apparently involves a dehydroboration–rehydroboration

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[1] It has been previously obtained, mp 142°, by the pyrolysis of tricyclooctylborane: R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3,** 174 (1964).

[2] E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90,** 5281 (1968).

[3] Such as, for example, H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90,** 1499 (1968); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90,** 818, 1911 (1968).

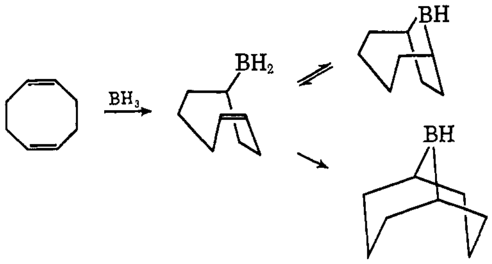
[4] (a) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84,** 190 (1962); (b) R. Köster, G. Griasnow, W. Larbig, and P. Binger, *Ann.*, **672,** 1 (1964); (c) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *Chem. Ind.* (London), 2087 (1962); (d) H. C. Brown and C. D. Pfaffenberger, *J. Am. Chem. Soc.*, **89,** 5475 (1967).

[5] The diol distribution was determined by converting the mixture to the diacetates and analyzing the diacetates by glpc using a 150 ft × 0.010 in. capillary column coated with poly(phenyl ether).

[6] A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72,** 1128 (1950), report mp 73.8–74.8°, bis-*p*-nitrobenzoate mp 181.4–182.8°.

[7] We have observed previously that isomerization of cyclooctylboranes appears to be unusually facile. Thus hydroboration–oxidation of 1-methylcyclooctene under the usual conditions leads to a mixture of products [H. C. Brown and G. Zweifel, *ibid.*, 83, 2544 (1961)] unless low temperatures and short reaction times are used [K. Varma, Ph.D. Thesis, Purdue University, 1967].

sequence,[8] the following mechanism (2) is indicated.



(2)

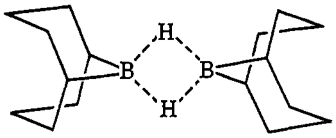
On simple thermodynamic consideration, it is easy to see that the 1,5 isomer, with two fused six-membered rings, should be more stable than the 1,4 isomer, with a seven-membered ring fused to a five-membered ring.

This makes possible an exceedingly simple preparative procedure. A 2-l. flask equipped with a reflux condenser, an addition funnel, a magnetic stirring bar, and a side arm fitted with a silicone rubber serum stopple was flushed with nitrogen and maintained under a static nitrogen atmosphere. In the flask was placed 800 ml of 1.0 *M* borane in THF and the flask was immersed in an ice bath. In the dropping funnel was placed 86.4 g (800 mmol) of 1,5-cyclooctadiene, made up to 200 ml with THF. The diene solution was added dropwise, with vigorous stirring, over a period of 20–30 min. The solution was then heated under reflux for 1 hr and then cooled to room temperature. A small amount of 9-BBN crystallized on cooling, leaving a saturated solution 0.78 *M* in the reagent. The crystalline compound was obtained by cooling the solution in an ice bath and filtering under nitrogen, followed by thorough washing with dry pentane. The yield of product in THF was essentially quantitative. The yield of crystalline material was approximately 65%.

9-Borabicyclo[3.3.1]nonane possesses the most remarkable thermal stability. Samples have been distilled at 195° (12 mm) or heated for 24 hr to 200° under nitrogen without loss of hydride activity or any noticeable change. This contrasts sharply with the behavior of other dialkylboranes, such as disiamylborane which isomerizes at 75°[9] or dicyclohexylborane which undergoes pyrolysis at 180–200° to yield cyclohexene and a polymeric borane.[10]

Even more unexpected, the white crystalline 9-BBN proved to be extraordinarily stable to air. A sample left in an open watch glass did not undergo any noticeable change over 24 hr. A bottle containing the product was opened at intervals over a 2-month period without appreciable loss of hydride activity. In spite of this unexpected inertness toward air, it exhibits the usual reactivity of a dialkylborane in hydroboration.[2] There are obviously major advantages in being able to store, weigh, and utilize such a reagent without the precautions required by the usual dialkylborane.

The infrared spectrum of 9-BBN, either as a THF solution or as a mineral oil mull, exhibits strong absorption at 1560 cm^{-1}, indicating the presence of a B–H–B bridge. Hence, 9-BBN must exist as the dimer (3), both in solution and in the crystalline state. The chair–chair conformation is selected in analogy to bicyclo[3.3.1]nonane, which exists in that conformation according to the X-ray analysis of Laszlo.[11] It has been reported that the C-3 and C-7 methylenes of bicyclo[3.3.1]nonanes will interact in the chair–chair conformation, giving rise to a characteristic infrared absorption at 1490 cm^{-1}.[12] Such absorption was observed in the spectrum of 9-BBN.



(3)

The boiling point of 9-BBN, 195° (12 mm), is unusually high. It should be contrasted with a boiling point of 98° (12 mm) for di-*n*-butylborane.[13] Simple dialkylboranes evidently dissociate and distil as the monomer, whereas 9-BBN must resist dissociation and distil largely as the dimer. Presumably dissociation would be accompanied by a widening of the C–B–C angle at the bridgehead to 120°. Such a widening could be readily accommodated in the acyclic dialkylborane such as di-*n*-butylborane, but would be resisted by the bicyclic structure. The unusual inertness toward oxygen may also be a reflection of the unusual stability of the boron–hydrogen bridge in these derivatives. Finally, we already have evidence that the exposed position of the boron atom at the bridge makes 9-BBN and its derivatives unusually effective in trapping carbanions, carbenes, and similar intermediates of value in applying the organoboranes for organic synthesis.[14]

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[8] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[9] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966).

[10] Köster[1] reports that the pyrolysis of tricyclohexylborane yields cyclohexene, cyclohexane, hydrogen, and a polymeric borane.

[11] I. Laszlo, *Rec. Trav. Chim.*, **84**, 251 (1965).

[12] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); W. A. C. Brown, G. Eglinton, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964).

[13] R. Köster, G. Bruno, and P. Binger, *Ann.*, **644**, 1 (1961).

[14] Research in progress with M. M. Rogić and M. W. Rathke.

[15] Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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9-Borabicyclo[3.3.1]nonane as a Convenient Selective Hydroborating Agent

Sir:

Dialkylboranes have many advantages over diborane itself for selective hydroborations.[1,2] The dialkylboranes previously applied, such as disiamylborane and dicyclohexylborane, have been quite sensitive to atmospheric oxygen. Consequently, they were commonly synthesized *in situ* prior to their application.[1,2]

We recently developed a simple procedure for the synthesis of 9-borabicyclo[3.3.1]nonane (9-BBN) *via* the cyclic hydroboration–isomerization of 1,5-cyclooctadiene.[3] The product, a crystalline solid, mp 140–142°, exhibited extraordinary thermal stability, as well as unusual stability (for a dialkylborane) toward atmospheric oxygen. It could readily be weighed and transferred in the open air. These properties indicated a promising future as a reagent provided it possessed the

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[1] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

[2] G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **85**, 2066 (1963).

[3] E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).