nated with 10% silver nitrate. The desired naturally derived Δ^{16} isomer **2e** melted at 108.5–110° after crystallization from methanol–ethyl acetate. The nmr, solution ir, and mass spectra (molecular ion peak at *m/e* 286) of this material were identical with the corresponding spectra of the hydrocarbon prepared from the product of cyclization of the tetraenic acetal.

Acknowledgment. We wish to 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.

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Received August 5, 1968

Asymmetric Induction of an Olefinic Acetal Cyclization

Sir:

The enzymatic cyclization of squalene proceeds with total asymmetric induction to produce only one enantiomeric form of the polycyclic products. It has been our general aim to simulate this result in our nonenzymic olefinic cyclizations.[1]

We have described the stannic chloride catalyzed cyclization of the *trans* dienic acetal **1** (R = H) which proceeds in high yield and essentially stereospecifically with respect to the ring fusion.[2] Thus when the reaction was conducted in nitromethane solution,[1] the major product (about 80% yield) was the *dl* mixture **2a,b** (R = CH_2CH_2OH). The *dl* mixture **3a,b** (R = CH_2CH_2OH), with the epimeric (equatorial) side chain, was the main constituent of the remainder of the product. Degradation of the side chain to the hydroxyl group, followed by oxidation, gave a single racemic ketone (**4a,b**) from both epimers. The present investigation was undertaken to see if the cyclization of the optically active acetal **1** (R = CH_3) derived from *l*-2,3-butanediol (*R,R* configuration) would proceed with asymmetric induction to produce, after the side-chain degradation, ketone that was rich in either **4a** or **4b**. This objective has been realized; indeed the degree of asymmetric induction observed was exceedingly high. We have been able, moreover, to ascertain the absolute configuration of the products.

The acetal **1** (R = CH_3) was prepared as follows. The *trans*-bromodiene **5**,[3] on condensation with sodiomalonic ester, gave the dienic malonic ester **6** (R = CO_2Et) which, upon heating with sodium cyanide in dimethyl sulfoxide,[4] suffered decarbethoxylation giving **6** (R = H). The alcohol **7**, obtained by reduction of **6** (R = H) with lithium aluminum hydride, was transformed in 94% yield into the corresponding aldehyde simply by treatment at room temperature for 15 min with about 6 mol equiv of Collins reagent.[5] This aldehyde, on treatment with excess *l*-butane-2,3-diol[6] in the presence of boron trifluoride etherate, was converted into the acetal **1** (R = CH_3), ORD $[\alpha]^{20}{}_{300}$ $-84.0°$ (*c* 0.699, dioxane).[7]

A solution of the acetal **1** (R = CH_3) (0.02 *M*) and stannic chloride (0.04 *M*) in benzene was allowed to stand for 7 min at room temperature. At the end of this period cyclization was complete. When nitromethane was used as the solvent cyclization was complete in 3 min at 0°. In pentane the reaction took about 4 hr at room temperature, and in ultradry pentane it required 9 days for completion.[8]

The major products of the cyclization, namely **2a,b** (R = $CH(CH_3)CH(OH)CH_3$) and **3a,b** (R = $CH(CH_3)$-$CH(OH)CH_3$), were easily separated by chromatography on Florisil. The side chain was removed very efficiently as follows: oxidation with Collins reagent[5] gave the corresponding keto ether (R = $CH(CH_3)COCH_3$) which, on treatment with lithium and ethylamine, underwent cleavage affording the octalols **2a,b** (R = H) and **3a,b** (R = H). Traces of impurities were removed from these last substances by submitting them to preparative tlc and vpc. In the case of the cyclization in benzene, the axial octalol **2a,b** (R = H), on oxidation with Jones reagent, yielded a specimen of octalone **4a,b**, ORD[9a] (*c* 0.261, dioxane) $[\Phi]_{589}$ $+118°$, $[\Phi]_{315}$ $+594°$, $[\Phi]_{222}$ $+9278°$, which, as shown below, corresponds to a composition of 92% **4b** and 8% **4a**. In contrast, the ORD curve of the octalone derived from the equatorial octalol proved to be the enantiomeric counterpart, corresponding to 8% **4b** and 92% **4a**.[9a] In the case of the cyclizations conducted in ultradry pentane and in nitromethane, the ORD curves of the octalones derived from the axial octalols indicated that **4b** was present to the extent of 86[9b] and 75%,[9a] respectively. These ORD curves were abnormal and could not be used to deduce the absolute configurations of the products.

The aforementioned enantiomeric ratios were determined as follows. A sample of axially derived octalone obtained from the cyclization in benzene was reduced by the Wolff–Kishner method and the pure *trans*-octalin was separated from the *cis* isomer[10] by preparative vpc. This octalin, in methanol, was treated with excess ozone at $-78°$ followed by hydrogen peroxide in acetic acid to give the keto acid **8** (R = CH_3).[11] Further oxidation with sodium hypobromite[12] afforded the diacid **8** (R = OH),[11] which was trans-

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[1] *Cf.* W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

[2] W. S. Johnson, A. van der Gen, and J. J. Swoboda, *J. Am. Chem. Soc.*, **89**, 170 (1967).

[3] S. F. Brady, M. A. Ilton, and W. S. Johnson, *ibid.*, **90**, 2882 (1968).

[4] A. P. Krapcho, G. A. Glynn, and B. J. Grenon, *Tetrahedron Letters*, 215 (1967).

[5] J. C. Collins, W. W. Hess, and F. J. Frank, *ibid.*, 3363 (1968).

[6] We wish to thank Dr. Karl L. Smiley, Head of Industrial Products Investigations, Fermentation Laboratory, U. S. Department of Agriculture, Peoria, Ill., for a generous gift of a sample of this material. The absolute configuration of this diol is known to be *R,R*; see, *inter alia*, L. J. Rubin, H. A. Lardy, and H. O. L. Fischer, *J. Am. Chem. Soc.*, **74**, 425 (1952).

[7] The optical activity was not attenuated upon prolonged extension of the time of reaction; hence no appreciable racemization of the optically active centers had occurred.

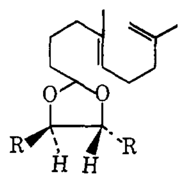
[8] The effect of traces of water to enhance the rate of reactions involving Lewis acid catalysts has been well documented: G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, pp 205–215.

[9] (a) Average of three determinations; (b) average of two determinations.

[10] The amount of *cis* isomer, formed during the Wolff–Kishner reaction (see ref 2), can be suppressed to about 20% by first conducting the hydrazone formation at 0° for 12 hr.

[11] As shown below, this substance contained about 92% of that enantiomeric form depicted by the formula.

[12] According to a modification of the procedure of C. Djerassi and J. Staunton, *J. Am. Chem. Soc.*, **83**, 736 (1961), in which the dioxane was omitted.



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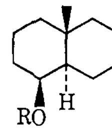

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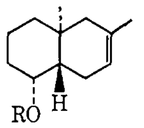

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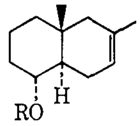

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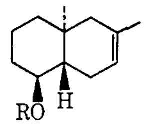

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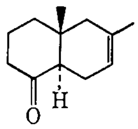

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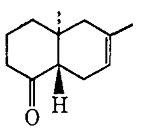

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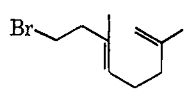

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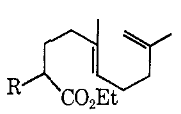

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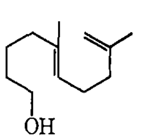

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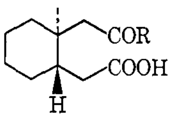

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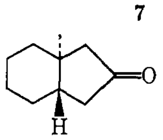

9

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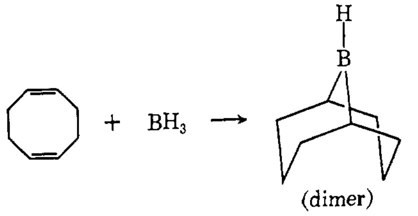
Cyclic Hydroboration of 1,5-Cyclooctadiene. A Simple Synthesis of 9-Borabicyclo[3.3.1]nonane, an Unusually Stable Dialkylborane

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 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)

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].