ever, an 86% yield of *n*-butylcyclopropane was obtained. Since the triple bond of 1-alkynes may be selectively hydroaluminated in the presence of double bonds,[18,19] it is thus conceivable that enynes containing a terminal acetylene group may be converted into alkenylcyclopropanes *via* the hydroalumination–methylenation reactions. We are currently exploring the feasibility of such transformations.

[18] V. V. Markova, V. A. Kormer, and A. A. Petrov, *Zh. Obshch. Khim.*, 37, 226 (1967); *J. Gen. Chem. USSR*, 37, 208 (1967); and preceding papers.

[19] G. Zweifel, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, 90, 7139 (1968); G. M. Clark, unpublished results.

[20] National Defense Education Act Fellow (Title IV) at the University of California, Davis, 1968–1970.

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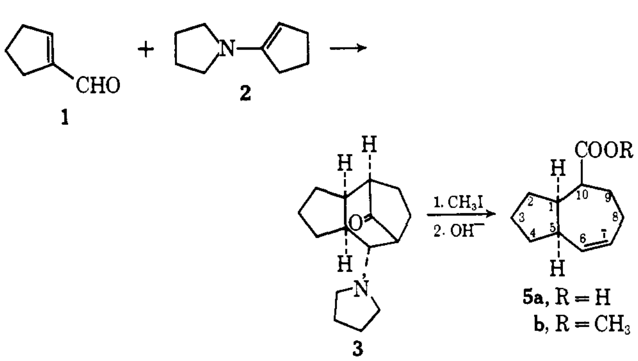
Sesquiterpenes. VI. A Short Stereospecific Synthesis of Functionalized Perhydroazulenes[1]

Sir:

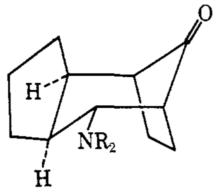
Simple stereospecific syntheses of perhydroazulenes are rare[1,2] and limited in applicability for creating models in conformational studies[3] or for constructing the many sesquiterpenes bearing this skeleton.[4] We offer here a new synthesis of this system which is short and stereospecific and produces in good overall yield a functionalized perhydroazulene capable of elaboration in many different ways. The central design principle in this synthesis is that, while medium rings cannot usually be constructed viably by cyclization, they can be made with facility through cleavages of bicyclic molecules composed of common-size rings. These bicyclics are in turn easily made by standard cyclization reactions. Stork's elegant reaction for creating bridged bicyclic ketones[5] is an excellent example, so far little exploited in synthesis, since he also showed the capability of the products for further cleavage to medium rings, with functions usefully sited on opposite sides of the ring.

We have utilized this principle in the construction of **3** from 1-cyclopentenylcarboxaldehyde[6] (**1**) and the pyrrolidine enamine of cyclopentanone (**2**). The reaction forms five asymmetric centers but its stereospecificity may be predicted from the presumption that the sequence of mechanistic steps includes no irreversible reactions. Hence the thermodynamically most stable product **3** should result; the 5–6 ring fusion has the more stable cis orientation and of the two cis forms, it should be the exo isomer which places axial substituents on opposite (rather than the same) sides of the chair cyclohexanone **4**.



1 **2** **3**

5a, R = H
b, R = CH$_3$



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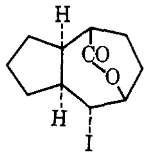

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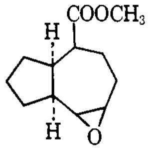

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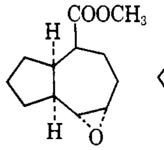

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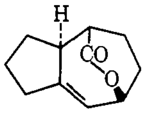

9

When the components **1** and **2** were allowed to stand 20 hr in dioxane at room temperature to form a crude amino ketone **3** and this (without isolation) was methylated with methyl iodide and boiled 3 hr with 15% aqueous alkali, up to 25% of crystalline bicyclic acid **5a** could be isolated [mp 68–70°; nmr τ −1.0 (s, 1), 4.25 (m, 2)].[7]

Proof of the stereochemistry of **5** was deduced from the easy formation of an iodolactone, **6**, mp 120°, on treatment of the acid **5a** in bicarbonate solution with iodine (as KI$_3$) at room temperature. The formation of a seven-ring lactone bridge is sterically impossible with a trans-fused 5–7 ring system. Of the two possible cis-fused isomers of **5** the one shown was selected since treatment of the iodolactone **6** with alkali followed by diazomethane esterification yielded epoxide **7** [bp 120° (bath temperature) (0.4 mm); nmr τ 6.45 (s, 3), 7.05 (t, 2, J = 3 Hz)], which in turn was the *minor* of two epoxides (1:3) formed on epoxidation of **5b** with perbenzoic acid. The epoxide formed from iodolactone **6** must possess a cis relation of epoxide and carboxyl so that the other, major epoxide, **8** [bp 130° (bath temperature) (0.5 mm); nmr τ 6.40 (s, 3), 7.07 (t, 1, J = 5 Hz), 7.38 (dd, 1, J = 5, 9.5 Hz)], from peracid must be the trans isomer. The preponderance of **8** in the peracid oxidation in turn implies peracid attack from the less hindered convex face of the bicyclic olefin and so a product **8** with epoxide cis to the ring juncture protons.[8]

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[1] Part V: J. B. Hendrickson, C. Ganter, D. Dorman, and H. Link, *Tetrahedron Lett.*, 2235 (1968).

[2] J. A. Marshall and W. F. Huffman, *J. Amer. Chem. Soc.*, 92, 6358 (1970), and references cited therein.

[3] Part IV: J. B. Hendrickson, *Tetrahedron*, 19, 1387 (1963).

[4] F. Sorm and L. Doleja, Ed., "Guaianolides and Germacroanolides," Holden-Day, San Francisco, Calif., 1960; "Selected Constants: Sesquiterpenoids," Pergamon Press, Elmsford, N. Y., 1966.

[5] G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, 78, 5129 (1956).

[6] J. B. Brown, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950).

[7] Spectra and analyses of all compounds reported were consistent with the assignments illustrated.

[8] This steric preference for the convex face is especially clear in Woodward's discussion of his reserpine synthesis.[9] The 3:1 predominance of **8** reported is only a minimum expression of steric preference since any direction of peracid cis to (and by) the ester group would produce the minor isomer **7**.

[9] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, 2, 1 (1958).

The structure of iodolactone **6** was further demonstrated by elimination of HI to form **9**, which occurred in hot base[10] when KI was added but not without KI addition. This implies that the only proton available for elimination is cis to iodine so that elimination is only effected after initial epimerization of iodide by iodide in an S$_N$2 displacement. The olefinic lactone **9** produced (bp 140°, 70 μm) shows only one vinyl proton (τ 4.33) in the nmr spectrum, consistent with the assigned structure **9**.

This synthetic sequence represents a readily available source of perhydroazulenes (25% overall yield to **5**, 20% overall to **9**) which is applicable to several conversions. Thus, *N*-bromosuccinimide on **9** affords a single secondary allylic bromide as a route to functionalizing the 5-ring. The typical three-carbon lactone appendages at C-7 in the guaianolide and pseudoguaianolide sesquiterpenes[4] are virtually always trans to the C-1 hydrogen and so can be stereospecifically introduced *via* cyclic intermediates from the (cis) carboxyl at C-10. One such procedure could be Claisen condensation of propionate ester with **8**, followed by internal displacement of the epoxide by the β-keto ester anion thus formed.[11]

The perhydroazulenes shown here are presently under investigation for conversion to pseudoguaianolides and conformational analysis models for cycloheptanes.

(10) The reaction required 96 hr at 115° in dimethylformamide with diazabicyclooctane (DABCO) as base (yield 91%); higher temperatures caused increasing reversion to acid **5b**.

(11) The epoxide **8** is very resistant to attack of external nucleophiles, presumably owing to the requisite axial position of the carboxyl at C-10 and the hindrance it offers to backside approach. We have not yet, however, tested the internal displacement.

(12) National Institutes of Health Predoctoral Fellow, 1969–1970.

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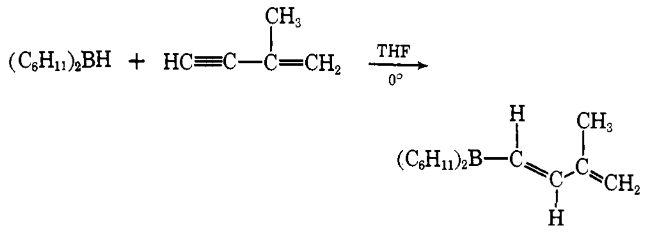
Synthetic Photochemistry of Organoboranes. The Photocyclization of Dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane

Sir:

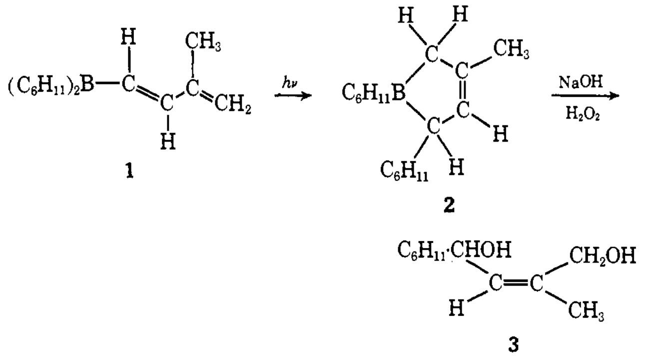
We wish to report that, upon ultraviolet irradiation, dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane (**1**) undergoes photocyclization to a boracyclopent-3-ene. This reaction is a new primary process in organoboron photochemistry, and also is of considerable interest as a synthetic route to a novel class of cyclic organoboranes.

The reaction of dicyclohexylborane with isopropenylacetylene at 0° for 2 hr in tetrahydrofuran solution gives dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane (**1**) in high yield and high isomeric purity.[1] The dienylborane exhibits an intense absorption maximum (ε 18,000) at 242 nm in tetrahydrofuran.



1

Irradiation of a 0.22 *M* solution of **1** in tetrahydrofuran for 6 hr under nitrogen using an unfiltered 450-W Hanovia lamp effected complete consumption of the dienylborane, as evidenced by disappearance of the dienylborane's terminal methylene nmr absorption at δ 5.22 concomitantly with the appearance of a new absorption at 5.5. Oxidation of the nearly colorless photolysate with alkaline hydrogen peroxide afforded a 58% isolated yield of 1-cyclohexyl-3-methyl-*cis*-2-butene-1,4-diol (**3**), mp 108–110°. It should be noted that at this time neither the photochemical nor the oxidative portions of the dienylborane–diol conversion have been optimized.



1 2 3

Assignment of structure **3** to the oxidation product is based on its elemental analysis, ir and nmr spectra, and ozonolysis products. Distinguishing features of the 60-MHz nmr spectrum of diol **3** (CD_3COCD_3 solution) are: (a) a doublet of multiplets at δ 5.33 (1 H, $-C(OH)H_\alpha CH_\beta{=}C(CH_{3\gamma})-$, $J_{\alpha,\beta} = 9$, $J_{\beta,\gamma} = 1.5$ Hz); (b) a multiplet centered at 4.11 containing an AB quartet (1 H, $-CH_\alpha<$; 2 H, $-CH_2OH$, $J_{AB} = 12.5$ Hz, $\Delta\delta_{AB} = 0.28$ ppm); and (c) a doublet at 1.82 (3 H, CH_3, $J_{\beta,\gamma} = 1.5$ Hz). The large coupling constant in the AB quartet, due to the asymmetry at C-1,[2] suggests the cis configuration of the double bond.[3] Ozonolysis of the diol **3** followed by sodium borohydride reduction gave 1,2-propanediol and cyclohexylethane-1,2-diol.

The structure of diol **3** strongly indicates that the photoproduct is *B*-cyclohexyl-2-cyclohexyl-4-methylboracyclopent-3-ene (**2**). Additional supporting evidence for the boron heterocycle structure **2** stems from its nmr spectrum in CCl_4 (δ 5.55, 1 H, m, and 0.7–2.1, m), the weak 1635-cm^{-1} C=C stretching frequency in its ir spectrum,[4] and from cryoscopic molecular weight determination in benzene.[5]

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(1) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Amer. Chem. Soc.*, in press.

(2) For a report on the effect of structure on magnetic nonequivalence due to molecular asymmetry, see, for example, G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

(3) The diacetate of **3** (n^{25}D 1.4687) has the methylene AB quartet centered at δ 4.63 (J = 12.5 Hz, $\Delta\delta_{AB}$ = 0.28 ppm), and has overlapping C-1 methine and H$_\beta$-vinylic proton absorptions at δ 5.2 (2 H, m).

(4) Conjugated vinylboranes exhibit a strong C=C stretching absorption at 1560–1610 cm^{-1}: G. M. Clark, C. C. Whitney, and G. Zweifel, unpublished observations.

(5) Removal of the solvent from the photoproduct followed by cryoscopic molecular weight determination gave an average molecular weight of 281, as compared to the expected molecular weight of 244 for the boracyclopentene **2**. This result establishes a monomeric species as the predominant photoproduct.