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 SN2 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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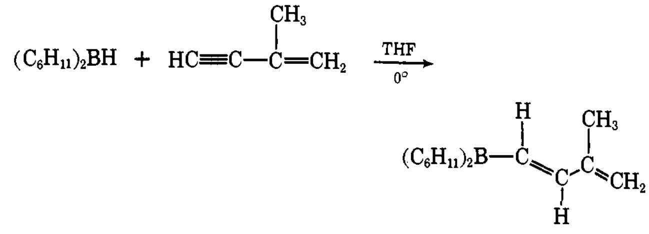
Synthetic Photochemistry of Organoboranes. The Photocyclization of Dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane

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.

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.



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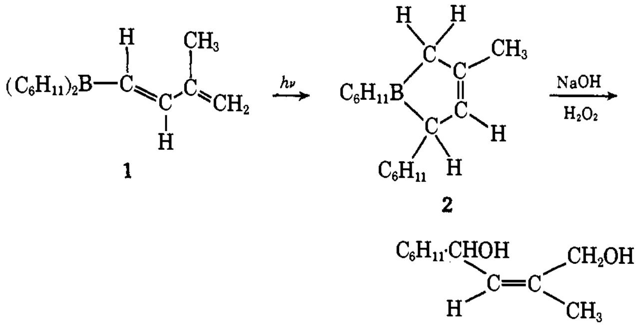


1 2 3

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, $\text{-C(OH)H}_\alpha\text{C}H_\beta\text{=C(CH}_{3\gamma}\text{)-}$, $J_{\alpha,\beta}$ = 9, $J_{\beta,\gamma}$ = 1.5 Hz); (b) a multiplet centered at 4.11 containing an AB quartet (1 H, $\text{-C}H_\alpha\text{<}$; 2 H, $\text{-C}H_2\text{OH}$, 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]

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

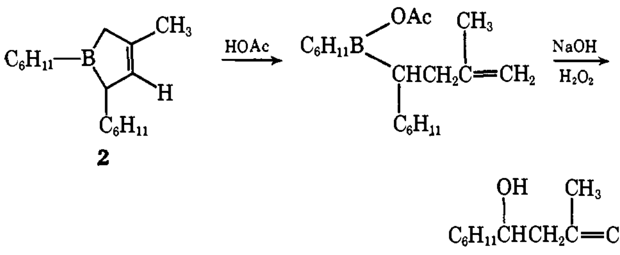
[2] For a report on the effect of structure on magnetic nonequivalence due to molecular asymmetry, see, for example, G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

[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_β-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.

Protonolysis of the boracyclopentene **2** with acetic acid followed by oxidation afforded 1-cyclohexyl-3-methyl-3-buten-1-ol (**4**) in 71% isolated yield.[6] The observed migration of the double bond in this reaction presumably takes place during the protonolysis of the organoborane.[7] It should also be noted that the double bond migrates exclusively in one direction.



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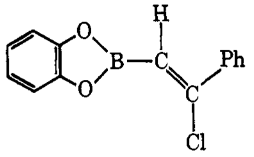
4

In view of the reported stability to ultraviolet irradiation of the vinylboranes **5**[8] and **6**[9], the deep-seated rearrangement of the dienylborane **1** is rather remarkable. Although the mechanistic details of the photoreaction are not yet known, it is apparent that both cyclization and migration of the cyclohexyl moiety from boron to the adjacent carbon must occur subsequently to an excited-state trans–cis isomerization. Whether cyclization and alkyl migration proceed in a concerted[10] or sequential[12] manner is a question we are currently attempting to answer.



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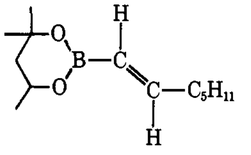

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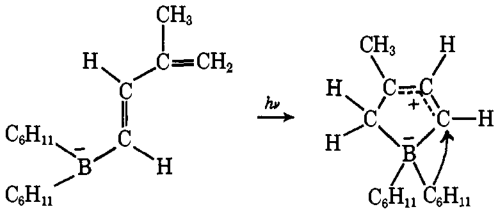

This discovery that dienylboranes undergo photocyclization opens a new area of synthetic and theoretical interest. We are continuing to explore the full scope of the photochemistry of vinyl- and dienylboranes.

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Oxidation Product of Bis(diphenylglyoximato)palladium(II) with Iodine[1]

Sir:

Recently the results of magnetic and X-ray studies on compounds of the type M(dpg)$_2$X, where X = I or Br, M = Ni(II) or Pd(II), and dpg stands for the anion diphenylglyoxime, were reported.[2] Our investigations on the electrical conductivity of solid transition metal complexes prompted us to prepare single crystals of the cited compounds using the earlier described procedures.[2,3a] In the case of Pd(dpg)$_2$I greenish needles with a remarkable metallic luster were obtained, in contradiction to the earlier statement of black reaction products.[2a,3] There is one other striking difference between Soderberg's findings and ours. A pure sample of the palladium–iodine complex did not show any esr absorptions even at liquid nitrogen temperature. The only observed effect during the study of the esr properties was a strong reduction of the cavity Q value by inserting the sample. This loss in reflected energy resembles in all respects the observations made after inserting finely dispersed metals into a cavity. This fact suggests in our opinion the presence of mobile conduction electrons in the solid complex Pd(dpg)$_2$I.

The formerly observed esr signals for this reason cannot be due to the proposed charge-transfer complex involving iodine and phenyl groups.[2a] The small amount of paramagnetic species found by Soderberg in Pd(dpg)$_2$I, and which always occurs in Ni(dpg)$_2$I, is, in our opinion, caused by lattice defects, where distinct paramagnetic, formally nickel(III) complex units cannot pair their free spins with neighboring ions. This explanation is supported by the earlier observed g values and their considerable anisotropy.[2a]

The results of far-ir[4] and uv investigations together with the above-mentioned physical properties led us to propose for these complexes a structure similar to those found in the iodine–starch compounds and related

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[6] Structure **4** was established from spectral data and elemental analysis and by direct synthesis from cyclohexanecarboxaldehyde and isobutenylmagnesium chloride.

[7] Migration of the double bond on hydrolysis of allylic boron derivatives has been previously reported: B. M. Mikhailov and A. Ya. Bezmenov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 904 (1965); H. C. Brown and H. Nambu, *J. Amer. Chem. Soc.*, **92**, 1761 (1970).

[8] M. Lappert and B. Prokai, *J. Organometal. Chem.*, **1**, 384 (1966).

[9] W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966).

[10] Concerted cyclization–migration would thus be the boron (uncoordinated) version of the $[\pi 4 + \sigma 2]$ cycloaddition–sigmatropic shift of a pentadienyl cation.[11]

[11] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[12] Cyclization (an allowed four-electron, excited-state disrotatory closure) may equally well be followed by migration of the cyclohexyl moiety from boron to carbon. The favored photochemical reaction pathway in tetraarylboronate complexes, for example, appears to involve aryl migration from tetracoordinate boron to the electron-deficient carbon.[13]

[13] J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, G. P. Happ, and D. P. Maier, *J. Amer. Chem. Soc.*, **90**, 53 (1968), and references therein.

[1] The investigation was supported by Deutsche Forschungsgemeinschaft, Bad Godesberg.

[2] (a) A. S. Foust and R. H. Soderberg, *J. Amer. Chem. Soc.*, **89**, 5507 (1967). (b) One of the reviewers kindly pointed out that neither this paper nor the earlier ones on this subject[2a,3] acknowledge the original preparation of these complexes by L. E. Edelman, *ibid.*, **72**, 5765 (1950). This work is remarkable at least in one respect, since Edelman emphasized for the first time the bronze, metallic sheen of the crystallized Ni(dpg)$_2$I.

[3] (a) M. Simek, *Collect. Czech. Chem. Commun.*, **27**, 337 (1962). (b) The olive green sheen of crystallized samples disappears after grinding the compound, giving rise to a dark brown, almost black, color.

[4] No I–I stretching vibration, which is typical for iodine charge-transfer complexes in the region of 200 cm^{-1}, and no metal–halogen vibration, typical for other oxidized bis(glyoximato)palladium(II) compounds, can be found.