[Contribution from the Bell Telephone Laboratories, Inc.]

Heterocyclic Organoboron Compounds. Some Derivatives of 1,3,2-Dioxaborole

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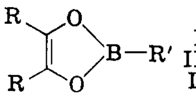
The preparation of 2-isopropyl-4,5-diphenyl- (II), 2-phenyl-4,5-dimethyl- (III), and 2-isopropyl-4,5-dimethyl-1,3,2-dioxaborole (IV) is reported. The ultraviolet absorption spectra of these compounds and 2,4,5-triphenyl-1,3,2-dioxaborole (I) are discussed. The conclusion is reached that the dioxaborole system can be thought of as a heterolog of the tropylium cation.

During the past few years, there has been a decided interest in the preparation of heterocyclic organoboron compounds in which the boron atom is an integral part of a potentially aromatic system. Most recently, the following systems have been synthesized: 2-phenyl-1,3-dihydro-2,1,3-benzoboradiazole[1] and the corresponding compounds in which one or both nitrogen atoms had been replaced with oxygen and/or sulfur,[2] 10-hydroxy-9-oxa-10-boraanthracene,[3] and dibenzo(*b,f*)borepin.[4]

Letsinger and Hamilton recently reported the synthesis of 2,4,5-triphenyl-1,3,2-dioxaborole (I)[5] and found that this compound exhibited an unusually high resistance toward hydrolysis for an ester of a boronic acid, and further that the ultraviolet absorption spectrum of I could not be explained as merely due to the *cis*-stilbene portion of the molecule. These workers suggested that the dioxaborole system might possess some degree of aromatic character.

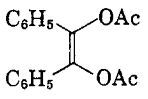


I. R, R' = C_6H_5
II. R = C_6H_5; R' = $CH(CH_3)_2$
III. R = CH_3; R' = C_6H_5
IV. R = CH_3; R' = $CH(CH_3)_2$

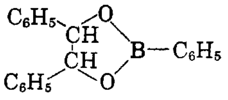
In view of the rather unusual properties of I, it was felt that the attempted preparation of dioxaborole systems containing alkyl rather than aryl substituents should be undertaken. The electronic absorption spectra of such compounds might shed some light on the nature of the aromatic character, if any, of these novel heterocyclic compounds.

The procedure employed for the synthesis of 2-isopropyl-4,5-diphenyl- (II), 2-phenyl-4,5-dimethyl- (III), and 2-isopropyl-4,5-dimethyl-1,3,2-dioxaborole (IV) parallels that employed by Letsinger and Hamilton in their synthesis of I.[5] It was observed that a phenyl substituent on the boron atom imparts a decided measure of stability toward air oxidation of these compounds, the order of stability being I > III > II > IV.

The structures assigned to compounds I to IV are consistent with the method of preparation and elemental analyses. In the case of compounds II, III, and IV, additional support for the structural assignments was obtained from a study of their NMR spectra.[6] Heterocycle II, aside from absorption due to the aromatic hydrogens, exhibited a doublet at $\tau = 8.82$ assigned to the methyl groups; III had a single line at $\tau = 8.02$ due to the methyl groups on the double bond. Compound IV has a doublet at 8.90 due to the isopropyl group methyl hydrogens and a single sharp line at 8.10 due to the olefinic methyl groups.



V



VI

An examination of the ultraviolet spectra of compounds I to IV is most revealing. As a point of reference, however, it should be stated that *cis*-stilbene-α,β-diol diacetate (V) has $\lambda_{\max}^{C_2H_5OH}$ 265 mμ ($\epsilon = 12{,}800$)[7] and *meso*-hydrobenzoin benzeneboronate (VI) has $\lambda_{\max}^{C_6H_{12}}$ 268 mμ ($\epsilon = 865$).[5] Clearly then, the spectra of I and II in cyclohexane (Figs. 1 and 2) are quite different from the spectra of V or VI, but in ethanol solution have absorptions similar to that of V. This change in absorption in going from cyclohexane to ethanol solution can be explained as resulting from coordination of the boron atom of I and II with the alcohol and thus essentially removing the boron from the π-electron system of the heterocyclic ring.[8] The ultraviolet spectrum of III (Fig. 3) is more significant. The absorption in cyclohexane cannot be due principally to the benzeneboronic ester moiety as seen

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(1) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, 80, 5411 (1958).

(2) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

(3) J. M. Davidson and C. M. French, *J. Chem. Soc.*, 191 (1960).

(4) E. E. van Tamelen, G. B. Brieger, and K. G. Untch, *Tetrahedron Letters*, No. 8, 14 (1960).

(5) R. L. Letsinger and S. B. Hamilton, *J. Org. Chem.*, 25, 592 (1960).

(6) The NMR spectra were determined in carbon tetrachloride on a Varian 60 mc. high resolution instrument. τ-Values are chemical shift values in p.p.m. relative to tetramethylsilane standard ($\tau = 10.00$).

(7) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., D. C. Heath and Co. (1957) p. 176.

(8) The possibility that the change in the spectrum in ethanol was due to a dissociation of the compounds to boronic acid and α-hydroxy ketone was considered. However, it was found that the spectrum of a mixture of benzoin and benzene boronic acid in ethanol was different from that of I.

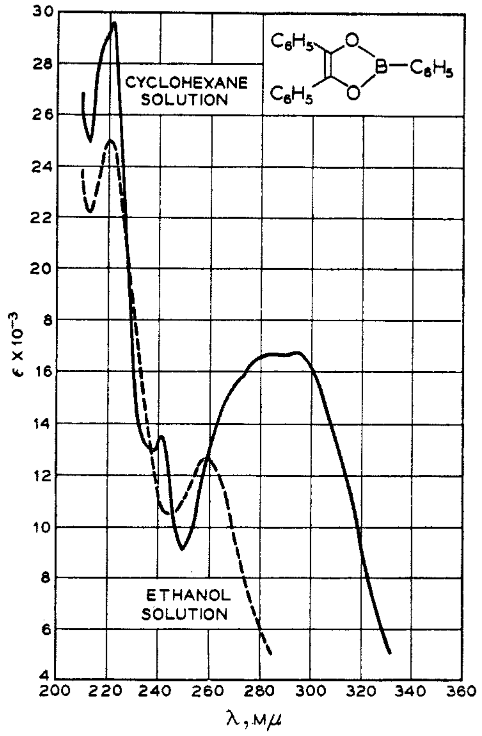

Figure 1

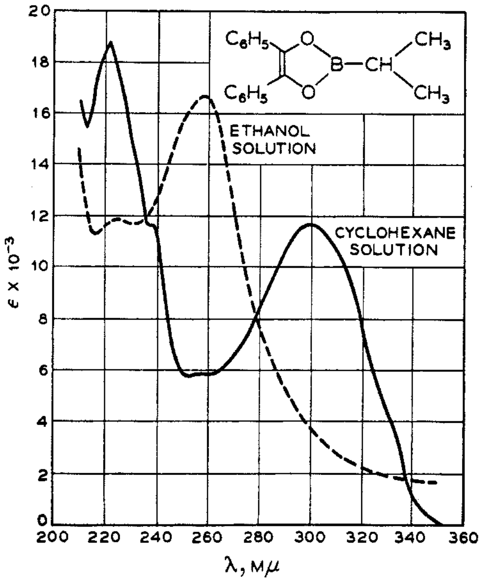

Figure 2

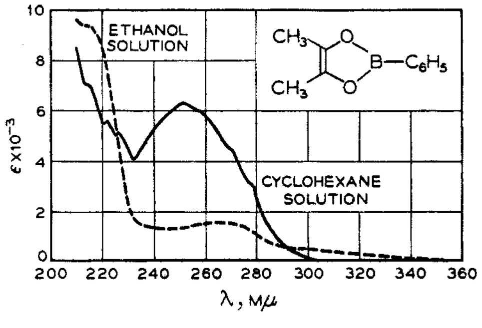

Figure 3

from a comparison with the spectrum of VI. However, in ethanol, the absorption of III shifts to one which can be associated entirely with that of a benzene derivative. Again the spectral shift observed in the two solvents emphasizes the importance of the boron atom in the π-electron system.

Because of the unusually small extinction coefficient (ϵ = 2.4) of the absorption band of IV (Fig. 4), the question arises as to whether or not this absorption is due to an impurity. That the spectrum is not the result of absorption by a decomposition product is borne out by the observation that the absorption of a cyclohexane solution of IV decreases with time so that after twenty-four hours only end absorption remains. An absorbing impurity which decomposes with time cannot be definitely ruled out. This is unlikely since (a) the change in the spectrum in ethanol is consistent with the shift observed in the spectra of I, II, and III and (b) the compound (III) obtained by substitution of a phenyl group on the boron atom possesses a new absorbing system whose spectrum reveals strong interaction between the heterocyclic ring and the benzene ring (Fig. 3). Furthermore, it is pertinent that other six π-electron systems also have relatively weakly absorbing long wavelength bands. For example, furan has ϵ = 1 at 252 mμ,[9] imidazole has ϵ = 60 at 250 mμ,[9] while benzene absorbs with an extinction of 250 in the region 255 mμ[9] and pyrrole absorbs at 340 mμ with ϵ = 300.[9] Only the thioanalogs, such as thiophene and thiazole have fairly intense absorption bands (235 mμ, ϵ = 4500; and 240 mμ, ϵ = 4000 respectively).[9] Substitution of the above compounds with phenyl groups increases the intensity of the absorption significantly; for example, biphenyl[9] has ϵ = 20,000 (246 mμ).[10] In view of these data, it seems that IV has a real ultraviolet absorption spectrum in the 303 mμ region of quite low intensity.

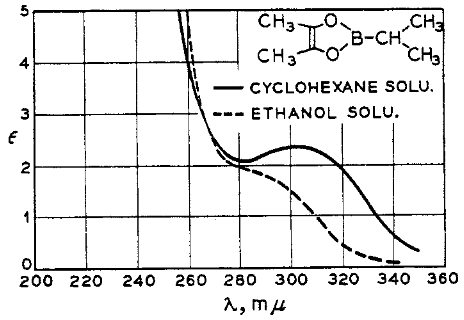

Figure 4

The spectra of compounds I to IV indicate that there is a strong interaction among the six π-electrons in the 1,3,2-dioxaborole system; these spectra cannot be attributed to the separate chromophores within the molecule and they support

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(9) A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy* Edward Arnold Ltd., London, 1958.

the expectation that this heterocyclic system would have spectral characteristics similar to those found in weakly aromatic systems such as furan. In this case, the empty *p*-orbital of the boron atom must be responsible for completion of the π-orbital network and thus 1,3,2-dioxaborole may be thought of as a heterolog of the tropylium cation.

EXPERIMENTAL[11]

2,4,5-Triphenyl-1,3,2-dioxaborole (I). This compound was prepared according to the directions of Letsinger and Hamilton.[5] The ultraviolet spectrum of I in cyclohexane was found to differ slightly from that reported by these authors.[5] I exhibited four maxima and a shoulder (——): (ϵ_{219} 29,000); ϵ_{222} 29,600; ϵ_{241} 13,500; ϵ_{283} 16,800; ϵ_{295} 16,800. In ethanol solution, I had but two maxima: ϵ_{221} 25,000; ϵ_{259} 12,700.

2-Isopropyl-4,5-diphenyl-1,3,2-dioxaborole (II). A benzene solution (250 ml.) containing 10 g. (0.11 mole) of 2-propaneboronic[12] acid and 24 g. (0.11 mole) of benzoin was heated for 20 hr. in a flask fitted with a take-off adapter to remove the water azeotrope. The benzene was removed at reduced pressure and the residue distilled (b.p. 140°/0.3 mm.) and then fractionated through a 2-ft. spinning band column to give 12 g. (40%) of a colorless liquid (b.p. 118°/0.2 mm.) which crystallized on standing, m.p. 46–47°. The ultraviolet spectrum in cyclohexane exhibited two maxima and two shoulders (——): ϵ_{222} 18,800; (ϵ_{239} 11,700); (ϵ_{257} 5850); ϵ_{299} 11,700. The spectrum in ethanol solution showed only two maxima: ϵ_{224} 11,900; ϵ_{258} 16,700.

Anal. Calcd. for $C_{17}H_{17}BO_2$: C, 77.28; H, 6.49. Found: C, 77.18; H, 6.70.

2-Phenyl-4,5-dimethyl-1,3,2-dioxaborole (III). Benzeneboronic acid (8 g., 0.07 mole) was allowed to react with practical grade 3-hydroxy-2-butanone (13 g., 0.15 mole) in 150 ml. of benzene as described above. Since the product was thermally sensitive, the crude material was distilled at 60–65°/0.7 mm. and then fractionated at 2 mm. (b.p. 79°). Although the product (6.6 g., 58%) crystallized on standing, analytical purity was not obtained until the compound was sublimed (40°/0.1 mm.); m.p. 46–47°.

The ultraviolet spectrum of III in cyclohexane contained four maxima and three shoulders (——): ϵ_{214} 7000; ϵ_{222} 5560; ϵ_{227} 5110; ϵ_{251} 6370; (ϵ_{260} 5830); (ϵ_{270} 4500); (ϵ_{277} 3050). In ethanol the spectrum exhibited two maxima and two shoulders (——): ϵ_{216} 9340; ϵ_{265} 1530; (ϵ_{273} 1430); (ϵ_{280} 1080).

Anal. Calcd. for $C_{10}H_{11}BO_2$: C, 69.02; H, 6.37. Found: C, 68.85; H, 6.32.

2-Isopropyl-4,5-dimethyl-1,3,2-dioxaborole (IV). 2-Propaneboronic[12] acid (28 g., 0.32 mole) was allowed to react with practical grade 3-hydroxy-2-butanone (28 g., 0.32 mole) in 300 ml. of benzene as described above. The benzene was removed at reduced pressure and the product distilled (b.p. 40–45°/15 mm.). Fractionation through a 2-ft. spinning band column yielded 9.1 g. (21%) of IV (b.p. 79–81.5°/90 mm).

The analytical sample had a b.p. of 81.5°/90 mm. and its ultraviolet spectrum in cyclohexane had one maximum, ϵ_{303} 2.4.

Anal. Calcd. for $C_7H_{13}BO_2$: C, 60.05; H, 9.36. Found: C, 60.26; H, 9.33.

Oxidation of IV. Approximately 250 mg. of IV was placed on a watch glass and allowed to stand exposed to the atmosphere. Within a few minutes, a white solid began to form around the edge of the liquid and the odor of biacetyl became very much apparent. The infrared spectrum (neat) of the oxidation product suggests the presence of 2-propaneboronic acid, biacetyl (1720 cm.$^{-1}$) and acetic anhydride (1760, 1825 cm.$^{-1}$).

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(10) Unfortunately the ultraviolet spectra of the monophenyl substituted furans have not been reported; however, those of the 2- and 3-*p*-chlorophenylfurans are recorded. Since the absorption of chlorobenzene (257 mμ, ϵ = 170)[9] is not significantly different from that of benzene (250 mμ, ϵ = 250),[9] it appears safe to assume that the spectra of the chlorophenylfurans are probably not markedly different from those of the phenylfurans. 2-*p*-Chlorophenyl- and 3-*p*-chlorophenylfuran have ϵ = 20,600 (287 mμ) and ϵ = 13,200 (262 mμ), respectively [A. W. Johnson, *J. Chem. Soc.*, 895 (1946)]. Here again we see the marked effect on the absorption intensity due to conjugation of a weakly absorbing system with a benzene ring.

(11) All melting points are corrected; boiling points are uncorrected. The ultraviolet spectra were determined with a Beckman DK-2 recording spectrophotometer.

(12) P. A. McCusker, E. C. Ashby, and H. S. Makowski, *J. Am. Chem. Soc.*, 79, 5179 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF PHARMACY, UNIVERSITY OF ILLINOIS]

Synthesis of Aminoisoxazolones from α-Cyano Esters and Hydroxylamine[1]

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The reaction of α-cyano esters with hydroxylamine afforded either 3-amino-5- or 5-amino-3-isoxazolones or α-amidoxime hydroxamic acids, depending on the reaction conditions. These products were characterized by their acetamido, benzamido, and arenesulfonamido derivatives.

The reaction of hydroxylamine with ethyl cyanoacetate has been reported by Modeen[2] to afford the amidoxime hydroxamic acid, $HONHCO{-}CH_2{-}C({=}NH)NHOH$. Further examination revealed this reaction to be more complex and a study of it was initiated using a number of α-cyano esters, I, ethyl cyanoacetate (R = H), ethyl α-cyano-β-methylvalerate (R = *sec*-butyl), ethyl α-cyano-α-cyclohexylacetate (R = cyclohexyl) and α-cyano-β-phenylpropionate (R = benzyl). From the reaction of each α-cyano ester with one mole of hydroxylamine in ethanol there were isolated two isomeric solids depending on the presence or absence of a

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(1) This work was presented before the Division of Organic Chemistry at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March 27, 1961.

(2) H. Modeen, *Ber.*, 27, (Referate) 261 (1894).