

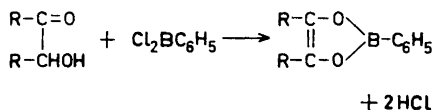
Short Communications

Heterocyclic Boron Compounds I

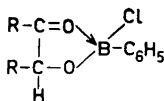
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In connexion with attempts to prepare boracycloheptatriene (borepin) and other heteroaromatic boron compounds it was found that acyloins (acetoin, propion, benzoin) react smoothly with phenylboron dichloride according to the following scheme:



probably with the following compound as an intermediate:

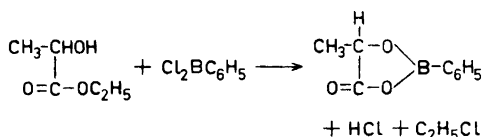


The compound derived from propion is a colourless liquid, whereas those derived from acetoin and benzoin form colourless crystals. They are all very sensitive to humidity and are hydrolysed to the acyloin and phenylboric acid. Attempts to prepare the benzoin derivative from phenylboric acid and benzoin were unsuccessful.

The above compounds are derivatives of a ring system 1,3-dioxa-2-boracyclopentene or 1,3,2-dioxaborole which might be considered a heteroaromatic system since the grouping $-\overset{+}{\text{B}}=\overset{-}{\text{O}}-$ is isoelectronic with the grouping $>\text{C}=\text{C}<$. The aromatic

stabilisation is, however, not significant. Dewar *et al.*¹ have prepared a similar derivative of catechol, which was also very sensitive to humidity.

Phenylboron dichloride also reacts with esters of α -hydroxyacids, such as ethyl lactate. In this case the reaction proceeds according to the scheme:



The resulting 2-phenyl-4-methyl-5-oxo-1,3,2-dioxaborolane is a colourless liquid which is extremely easily hydrolysed so that special care has to be taken to avoid hydrolysis when it is handled.

The infrared spectrum of this compound (in CCl_4 solution) shows a strong band at 1803 cm^{-1} , corresponding to a lactone $\text{C}=\text{O}$ group, but no absorption above 3050 cm^{-1} . Accordingly the compound must have the structure assigned to it above; no tautomerisation to the 5-hydroxydioxaborole seems to occur.

The infrared spectra of the acyloin derivatives show no absorption in the double bond region. This seems to indicate that the dioxaborole ring system has some aromatic character irrespective of chemical reactivity. All the heterocyclic boron compounds studied show strong absorption bands at $1440-1445\text{ cm}^{-1}$ ($\text{C}_6\text{H}_5-\text{B}$), $1365-1375$ and $1310-1320\text{ cm}^{-1}$ ($\text{B}-\text{O}$) and $1240-1270\text{ cm}^{-1}$ ($\text{C}-\text{O}-$).

Similar S- and N-containing compounds are being studied.

EXPERIMENTAL

General procedure. A solution of phenylboron dichloride (0.1 mole) in dry methylene chloride (100 ml) was placed in a three-necked flask

provided with a precision-ground stirrer, a reflux condenser with a CaCl_2 -tube and a dropping funnel with a pressure-equalising tube. A solution of the acyloin (0.1 mole) in methylene chloride (100-400 ml, see below) was added through the dropping funnel in the course of 1 1/2 h while a stream of dry nitrogen was passed through the apparatus from an inlet in the dropping funnel. Finally the solution was refluxed for 1 h. The hydrogen chloride evolved was collected in water and titrated with sodium hydroxide; usually a titer close to 95 % of the theoretical was found.

After the solution had been refluxed, the reflux condenser was replaced by a Claisen head with condenser and the solvent was distilled off. The triphenyl derivative crystallised; it was recrystallised from acetone. The other compounds were distilled *in vacuo*, moisture being carefully prevented from passing into the apparatus.

2,4,5-Triphenyl-1,3,2-dioxaborole. From 21.2 g of benzoin dissolved in 400 ml of methylene chloride. Recrystallised from dry acetone. Yield 16.7 g = 58 %. M.p. 110.5–111°C. (Found: C 79.80; H 5.05. Calc. for $\text{C}_{20}\text{H}_{15}\text{BO}_2$: C 80.50; H 5.07).

2-Phenyl-4,5-diethyl-1,3,2-dioxaborole. From 11.6 g of propion in 100 ml of methylene chloride. Yield 10.0 g = 50 %. B.p./11 mm: 118–19°C. (Found: C 71.20; H 7.50. Calc. for $\text{C}_{12}\text{H}_{15}\text{BO}_2$: C 71.34; H 7.43).

2-Phenyl-4,5-dimethyl-1,3,2-dioxaborole. From 8.8 g of dimeric acetoin dissolved in 250 ml of methylene chloride. The reaction product, which boiled from 119 to 129°C at 11–12 mm Hg, crystallised on standing; it was recrystallised from pentane. Yield 9.3 g = 53 %. M.p. 43.5–44.5°C. The compound was very sensitive to humidity, and we did not succeed in obtaining quite correct analytical values. (Found: C 67.20; H 6.63. Calc. for $\text{C}_{10}\text{H}_{11}\text{BO}_2$: C 69.02; H 6.37).

2-Phenyl-4-methyl-5-oxo-1,3,2-dioxaborolane. From 11.8 g of ethyl lactate in 125 ml methylene chloride. Yield 8 g = 46 %, distilling from 127 to 128°C at 11 mm Hg. (Found: C 61.50; H 5.38. Calc. for $\text{C}_9\text{H}_9\text{BO}_3$: C 61.42; H 5.35).

1. Dewar, M. J. S., Kuppa, V. P. and Pettit, R. *J. Chem. Soc.* 1958 3073, 3076.

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The Structure of β -Lyxose

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In 1947 Hassel and Ottar¹ advanced the assumption that the six membered pyranose ring is chair formed. The correctness of this assumption has been confirmed by the determination of several pyranose structures²⁻⁶. The chair formed pyranose ring, however, made it necessary to accept two possible structures for each pyranose isomer, one being formed from the other by a conversion of the ring. The existence of only one of the conversion forms of a pyranose in the crystalline state seems to be due to their different stability, and the hexa- and penta-pyranoses which so far have been determined²⁻⁶ agree with the proposals of Reeves⁷.

The purpose of the present work is to find out whether the same is valid for β -lyxose. This pentapyranose has the conversion forms *1e2a3e4e* and *1a2e3a4a*. According to Reeves' stability scheme the first form is the more stable, and is consequently expected to be found in β -lyxose crystals.

Crystallization of β -lyxose was tried from several different solvents, but always resulted in syrups. Eventually one crystal large enough for single crystal studies was obtained by placing some syrup on an objective glass and then making scratches in the glass. The crystals grown in this way are needle-shaped and elongated along the *c* axis.

Space group and axial lengths were determined from Weissenberg and oscillation photographs, using $\text{CuK}\alpha$ radiation. The crystals are orthorhombic and the space group is $P2_12_12_1$. The unit cell dimensions are, $a = 9.58 \text{ \AA}$, $b = 10.42 \text{ \AA}$ and $c = 6.53 \text{ \AA}$, to within 0.5 %. With four molecules in the unit cell the calculated density is 1.53 g/cm³, which agrees with the experimental value 1.54 g/cm³.

The intensities of the $hk0$ reflections were estimated visually from a series of Weissenberg photographs, using an intensity scale made from one of the reflections in this zone. 67 $hk0$ reflections were observed, representing about 52 % of the possible number observable under the experimental conditions. The intensities were corrected for the Lorenz and polarization factors in the usual way, and in order to derive the