

SHORT  
COMMUNICATIONS

## Reaction of Acetonitrile with Cyclic Boronic Esters Derived from *cis*-Acenaphthenediol

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Reactions of six-membered cyclic boronic esters with acetonitrile are known to give the corresponding 5,6-dihydro-4*H*-1,3-oxazines [1–3]. In the present communication we report on a similar transformation of five-membered cyclic boronic esters, 2-alkylacenaphtho[1,2-*d*][1,3,2]dioxaborolanes **I** and **II**, into 2-methyldihydrooxazole derivative **III**. The reaction is accompanied by partial hydrolysis of **III** to 1-amino-2-hydroxyacenaphthene (**IV**).

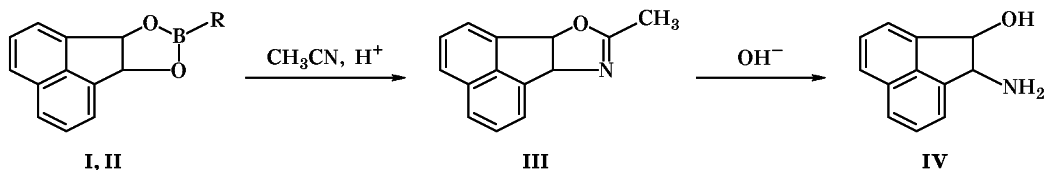
The composition of a mixture of products **III** and **IV** (TLC) and the structure of the components were confirmed by the IR and mass spectra. The mass spectrum contained the molecular ion peaks of compounds **III** and **IV** with *m/z* values of 209 and 185 and relative intensities of 14% and 32%, respectively. Also, an ion peak with *m/z* 168 (100%) was observed, which corresponds loss of acetonitrile molecule from the molecular ion of **III** or of NH<sub>3</sub> molecule from the molecular ion of **IV**. In the IR spectrum of mixture **III/IV** strong bands at 3300 (OH, NH), 1660 (C=N), and 1600 cm<sup>-1</sup> (C=C<sub>arom</sub>) were present. Treatment of the product mixture (0.11 g) with aqueous potassium hydroxide gave amino alcohol **IV** (0.1 g) which was isolated as a dark brown powder, decomposing above 180°C. This reaction supports the general character and mechanism of transformation of cyclic boronic esters into N-heterocycles [3] and provides a new route to 1,2-aminoalcohols.

Initial esters **I** and **II** were synthesized by reaction of the corresponding acyclic boronic esters [4] with *cis*-1,2-dihydroxyacenaphthene [5] according to the general procedure described in [6].

**2-Isopropyl-3a,9b-dihydroacenaphtho[1,2-*d*]-[1,3,2]dioxaborole (I)**. Yield 60%, oily liquid. <sup>1</sup>H NMR spectrum, δ, ppm: 0.87 d [6H, (CH<sub>3</sub>)<sub>2</sub>, *J* = 6.8 Hz], 1.79 m (1H, CHB), 6.07 s (2H, CHO), 7.61 m (6H, H<sub>arom</sub>). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 238 (35) *M*<sup>+</sup>, 152 (100) [*M*-C<sub>3</sub>H<sub>7</sub>BO<sub>2</sub>]<sup>+</sup>.

**2-Isobutyl-3a,9b-dihydroacenaphtho[1,2-*d*]-[1,3,2]dioxaborole (II)**. Yield 60%, mp 67–68°C (from benzene). <sup>1</sup>H NMR spectrum, δ, ppm: 0.80 d (2H, BCH<sub>2</sub>, *J* = 7.2 Hz), 0.86 d [6H, (CH<sub>3</sub>)<sub>2</sub>, *J* = 6.6 Hz], 1.83 m (1H), 6.10 s (2H, CHO), 7.61 m (6H, H<sub>arom</sub>). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 252 (44) *M*<sup>+</sup>, 152 (100) [*M*-C<sub>4</sub>H<sub>9</sub>BO<sub>2</sub>]<sup>+</sup>.

**Reactions of cyclic boronic esters I and II with acetonitrile.** Concentrated sulfuric acid, 10.6 ml (0.2 mol), was slowly added in a dropwise manner to a solution of 0.01 mol of compound **I** or **II** in 150 ml of acetonitrile, and the mixture was refluxed for 4 h (on a water bath). Excess acetonitrile was distilled off on a rotary evaporator, and the viscous residue was diluted with 100 ml of water and extracted with chloroform (2 × 50 ml). The aqueous phase was treated with solid sodium hydroxide to pH 9–10 on cooling



**I**, R = *iso*-C<sub>3</sub>H<sub>7</sub>; **II**, R = *iso*-C<sub>4</sub>H<sub>9</sub>.

with ice, the precipitate was filtered off, and the filtrate was extracted with chloroform (4 × 50 ml); the solvent was removed from the extract, and the residue was combined with the precipitate. We thus isolated 0.5 g of a mixture of compounds **III** and **IV** to which 50 ml of 25% aqueous potassium hydroxide was added, and the mixture was refluxed for 3 h. It was extracted with chloroform (2 × 25 ml), and the extract was evaporated to obtain amino alcohol **IV**.

The mass spectra (70 eV) were obtained on an MKh-1321 instrument. The <sup>1</sup>H NMR spectra were recorded on a Bruker AM-250 spectrometer from 10% solutions in CDCl<sub>3</sub> containing TMS as internal reference. The IR spectra were measured on a Specord 75IR instrument in mineral oil. TLC analysis was performed on Silufol UV-254 plates (eluent benzene–chloroform, 1 : 1; development with iodine vapor).

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