Russian Journal of General Chemistry, Vol. 71, No. 5, 2001, pp. 817-818. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 5, 2001, pp. 870–871.

LETTERS TO THE EDITOR

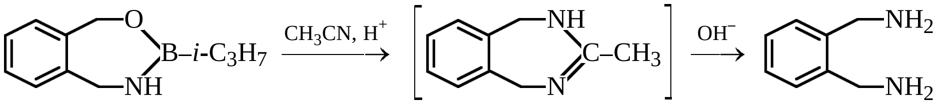
Reaction of 2-Isopropyl-5,6-benzo-1,3,2-oxazaborepane with Acetonitrile

V. V. Kuznetsov, Yu. E. Brusilovskii, and A. V. Mazepa

Bogastskii Physicochemical Institute, National Academy of Sciences of Ukraine, Odessa, Ukraine
Ufa State Petroleum Technical University, Ufa, Bashkortostan, Russia

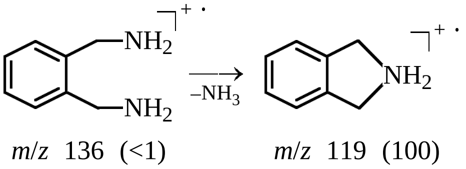
Received July 10, 2000

Reaction of substituted 1,3,2-dioxaborinanes with acetonitrile yields the corresponding 2-methyl-5,6-dihydro(4*H*)-1,3-oxazines [1, 2]. Under the same conditions 2-isobutyl-4,6,6-trimethyl-1,3,2-oxazaborinane converts to 2,4,6,6-tetramethyl-1,4,5,6-tetrahydropyrimidine [3]. Here, with 2-isopropyl-5,6-benzo-1,3,2-oxazaborepane **I** as example, we showed for the first time that seven-membered cyclic borates of amino alcohols can undergo a similar transformation to give 1,2-diaminomethylbenzene **III**, the product of hydrolysis of the intermediate 2-methyl-3,4-dihydro-1,3-benzodiazepine **II**.



I **II** **III**

Compound **II** was not isolated, apparently because of its high tendency to hydrolysis. Diamine **III** was obtained in a 65% yield as a dark red oil with a characteristic odor. Its composition and structure were confirmed by ^{1}H NMR and IR spectroscopy and mass spectrometry. The ^{1}H NMR spectrum contains the characteristic signals of all the groups of protons, δ, ppm: 1.15 s (4H, NH_2), 3.49 s (4H, CH_2–N), and 6.99 s (4H, C_6H_4). The IR spectrum contains strong bands at 3280 (ν_{NH}) and 1540 cm^{-1} ($\nu_{CC_{arom}}$). The mass spectrum contains a peak of an ion with *m*/*z* 119, which is the most intense and corresponds to fragmentation of M^+ [4].



m/*z* 136 (<1) *m*/*z* 119 (100)

Along with **III**, an unidentified crystalline red-brown substance was isolated from the reaction mixture. It decomposes on heating above 270°C; the highest *m*/*z* value in its mass spectrum is 248 (5).

The discovered reaction evidently proceeds by the mechanism similar to that observed for six-membered cyclic esters of boric acid [5]; it is a fairly convenient route to the corresponding 1,4-diamines.

The initial cyclic boronic ester **I** was prepared by the reaction of 1-hydroxymethyl-2-aminomethylbenzene [6] with dibutyl isopropylboronate, following the general procedure [2], as a dark red oil in a 53% yield. IR spectrum, ν, cm^{-1}: 3150 (ν_{NH}), 1600 ($\nu_{CC_{arom}}$). ^{1}H NMR spectrum, δ, ppm: 0.90 d (6H), 1.42 m (1H), 3.09 s (1H), 3.53 s (2H), 3.71 s (2H), 7.21 s (4H). Mass spectrum, *m*/*z* (I_{rel}, %): 189 (18) $[M]^+$, 146 (71) $[M - C_3H_7]^+$, 119 (100) $[M - C_3H_7 - BNH_2]^+$. To a solution of 0.006 mol of this compound in 100 ml of acetonitrile, 0.2 mol of concentrated sulfuric acid was slowly added dropwise with stirring. After that the reaction mixture was refluxed on a water bath for 5 h, excess acetonitrile was removed on a rotary evaporator, and the viscous residue was diluted with 100 ml of water and extracted with chloroform (2 × 50 ml). The remaining aqueous phase was cooled with ice and alkalized with solid NaOH to pH 9–10. The resulting red-brown residue of an unidentified compound was filtered off (yield 0.21 g), and the aqueous phase was extracted with chloroform (4 × 50 ml). After removing the solvent, 0.53 g of diamine **III** was isolated.

1070-3632/01/7105-0817 $25.00 ©2001 MAIK "Nauka/Interperiodica"

The ^{1}H NMR spectra were measured on a Tesla BS-497 spectrometer with 15% solutions in C_6D_6 for **III** and in $CDCl_3$ for **I** against internal TMS. The IR spectra were recorded on a Specord-75 IR spectrometer in thin layer. The mass spectra were obtained on an MKh-1321 spectrometer with the ionizing electron energy of 70 eV.

REFERENCES

1. Kuznetsov, V.V., *Zh. Org. Khim.*, 1994, vol. 30, no. 10, p. 1571.
2. Kuznetsov, V.V. and Shvets, V.N., *Zh. Org. Khim.*, 1997, vol. 33, no. 10, pp. 1577–1579.
3. Kuznetsov, V.V., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 6, pp. 1040–1041.
4. Vul'fson, N.S., Zaikin, V.G., and Mikaya, A.I., *Mass-spectrometriya organicheskikh soedinenii* (Mass Spectrometry of Organic Compounds), Moscow: Khimiya, 1986, p. 130.
5. Kuznetsov, V.V., *Teor. Eksp. Khim.*, 2000, vol. 36, no. 3, pp. 159–161.
6. Kusnetsov, V.V., Brusilovskii, Yu.E., Mazepa, A.V., and Krasnoshchekaya, S.P., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, pp. 164–165.