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REACTION OF SEVEN-MEMBERED CYCLIC BORIC ESTERS WITH ACETONITRILE

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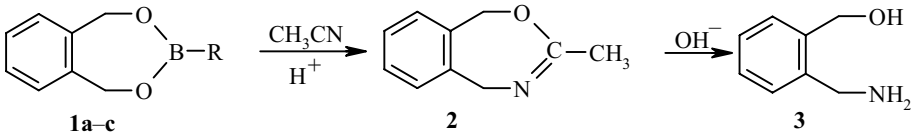
Five- and six-membered cyclic boric esters form 1,3-oxazolines and 5,6-dihydro(4H)-1,3-oxazines on reaction with acetonitrile [1-3]. In this paper it is shown, using 2-substituted 5,6-benzo-1,3,2-dioxaborepanes (**1a-c**) as examples, that the analogous conversion of seven-membered cyclic boric esters into 2-methyl-3,4-dihydro-1,3-benzoxazepines (**2**) and the product of their hydrolysis, 1-hydroxymethyl-2-aminomethylbenzene (**3**), is possible.



1a–c **2** **3**

1a R = C_2H_5; **b** R = *i*-C_3H_7; **c** R = *i*-C_4H_9O

This reaction is a new example of the chemical reactions of the poorly studied class of seven-membered cyclic boric esters. It opens a new route to the synthesis of 1,3-benzoxazepines and 1,4-amino alcohols. Thus, on stirring and slowly adding conc. H_2SO_4 (1.6 ml, 0.2 mol) to a solution of esters **1a-c** (0.01 mol) in acetonitrile (60 ml) with subsequent boiling for 3 h at about 100°C, dilution with water (100 ml), extracting with chloroform (2 × 50 ml), treatment of the aqueous phase with ice and LiOH to pH 9-10, and filtration of the precipitate, oxazepine **2** was obtained as colorless crystalline compound, which decomposed on heating above 185°C, in yields of 25% (from **1a**), 33% (from **1b**), and 24% (from **1c**).

2-methyl-3,4-dihydro-1,3-benzoxazepine (2). ^{1}H NMR spectrum (Tesla BS 497, $CDCl_3$, TMS), δ, ppm: 1.91 (3H, s, CH_3); 4.10 (2H, s, OCH_2); 4.22 (2H, s, N-CH_2); 7.19 (4H, s, H_{arom}). Mass spectrum (MX-1312, 70 eV), *m/z*, (*I*, %): [M^+] 161 (70), [M - CH_3CNH] 119 (100). Extraction of the aqueous filtrate with chloroform (4 × 50 ml) amino alcohol **3**, containing a small amount of compound **2** was isolated (43-50% yield). Compound **3** was purified by boiling for 4 h with 30% aqueous KOH (15 ml), extraction with chloroform (3 × 10 ml), and removal of the solvent in vacuum. The yield of compound **3** by hydrolysis of the previously prepared benzazepine **2** was 70%.

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2-Aminomethyl-1-hydroxymethylbenzene (3). IR spectrum, ν, cm^{-1}: 3450-3290 (OH, NH), 1580 and 1510 (C=C arom.). Mass spectrum, *m/z* (*I*, %): $[M^+ - H_2O]$ 119 (100). The starting compounds **1a-c** were prepared by reaction of the corresponding acyclic boric esters with 1,2-di(hydroxymethyl)benzene by a known method [4].

2-Ethyl-5,6-benzo-1,3,2-dioxaborepane 1a (oil) was isolated in 85% yield. ^{1}H NMR spectrum, δ, ppm: 0.70 (3H, t); 0.87 (2H, q); 5.01 (4H, s); 7.22 (4H, s). Mass spectrum, *m/z*, (*I*, %): $[M^+]$ 176 (95), $[M - C_2H_5]^+$ 147 (52), $[M - C_2H_5 - HBO]^+$ 119 (53), $[M - C_2H_5 - CH_2O]^+$ 117 (73).

2-Isopropyl-5,6-benzo-1,3,2-dioxaborepane 1b was obtained in 69% yield; mp 60-62°C (benzene). ^{1}H NMR spectrum, δ, ppm: 0.83 (7H, s); 5.00 (4H, s); 7.21 (4H, s). Mass spectrum, *m/z* (*I*, %): $[M^+]$ 190 (67), $[M - C_3H_7]^+$ 147 (59), $[M - C_3H_7 - CH_2O]^+$ 119 (25), $[M - C_3H_7 - HBO]^+$ 117 (48), $[M - C_3H_5B(OH)_2]^+$ 104 (100). During the synthesis of esters **1a,b** the formation of a small amount of boron containing polymer (less than 10% of the mass of the principal product) was observed.

2-Isobutoxy-5,6-benzo-1,3,2-dioxaborepane 1c (oil) was obtained in 70% yield. ^{1}H NMR spectrum, δ, ppm: 0.82 (6H, d); 1.71 (1H, m); 3.51 (1H, m); 4.85 (4H, s); 7.22 (4H, s). Mass spectrum, *m/z* (*I*, %): $[M]^+$ 220 (13), $[M - C_3H_7]^+$ 177 (100), $[M - C_3H_7 - CH_2O]^+$ 147 (50), $[M - C_4H_9OB(OH)_2]^+$ 104 (63).

REFERENCES

1. V. V. Kuznetsov, *Abs. Ukraine Conf. "Chemistry of Nitrogen Heterocycles"* [in Ukrainian]. 1997, 50.
2. V. V. Kuznetsov, *Zh. Org. Khim.,* **30**, 1571 (1994).
3. V. V. Kuznetsov and V. N. Shvets, *Zh. Org. Khim.,* **33**, 1577 (1997).
4. V. V. Kuznetsov, A. V. Mazepa, and L. V. Spirikhin, *Khim. Geterotsikl. Soedin.,* 1418 (1998).