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The preparation of some 2-substituted-4*H*-1,3,2-benzothioxaborine and 2-substituted-1*H*,4*H*-1,3,2-benzazoxaborine is described.

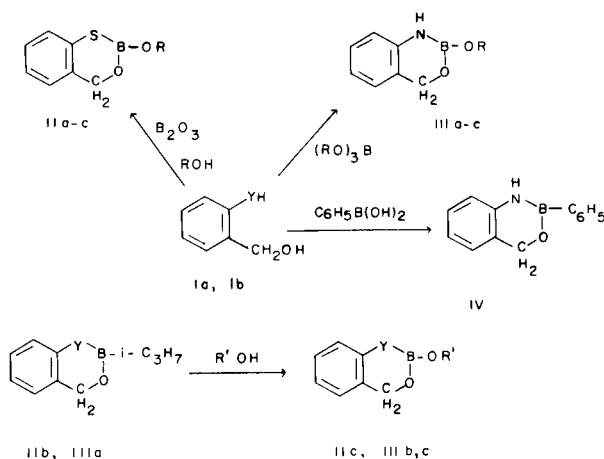
J. Heterocyclic Chem., **19**, 297 (1982).

Five-membered ring benzo-derivatives containing an O-B-S linkage have been previously reported (1), however, analogous six-membered ring compounds are unknown.

Six-membered ring benzo-derivatives with O-B-N linkage (such as 2-substituted-3*H*,4*H*-1,3,2-benzoxazaborine) have been previously studied (2), while the analogous 2-substituted-1*H*,4*H*-1,3,2-benzazoxaborine isomers are unknown. In this preliminary paper, the preparation of 2-substituted-4*H*-1,3,2-benzothioxaborine and 1*H*,4*H*-1,3,2-benzazoxaborine is described.

The reactions involved are shown in the Scheme 1. Derivatives IIa-c, IIIa-c and IV are thermally stable and can be distilled under reduced pressure, but all the compounds spontaneously hydrolyze in the presence of moisture. Derivatives IIc and IIIb,c can be obtained by exchange reaction between IIb, IIIa and *n*-butyl alcohol or phenol.

Scheme 1



Ia: Y = S, Ib: Y = NH

IIa: Y = S, R = C₂H₅; IIb: Y = S, R = *i*-C₃H₇; IIc: Y = S, R = C₆H₅IIIa: R = *i*-C₃H₇; IIIb: R = *n*-C₄H₉; IIIc: R = C₆H₅IV: R = C₆H₅R' = *n*-C₄H₉, C₆H₅

EXPERIMENTAL

Literature procedures were followed in the preparation of 2-mercapto-benzyl alcohol Ia (3) and 2-aminobenzyl alcohol Ib (4). All the operations involved in the preparation, transfer and distillation of IIa-c, IIIa-c and IV were carried out in an atmosphere of dry oxygen-free nitrogen. Melting points were determined on a Tottoli apparatus and are uncorrected. The nmr spectra were recorded on a Varian FT 80 A spectrometer with TMS as internal standard. Microanalysis for C, H, N, and S were carried out on a Carlo Erba model 1106 Elemental Analyser. Boron was estimated by Thomas method (5).

2-Ethoxy-4*H*-1,3,2-benzothioxaborine (IIa).

Boric oxide (0.012 mole), ethanol (0.024 mole) and 2-mercaptobenzyl alcohol (0.024 mole) were refluxed in benzene (120 ml) using a Dean-Stark apparatus, until the stoichiometric amount of water was eliminated. The solvent was removed under vacuum and the residue afforded on distillation 2-ethoxy-4*H*-1,3,2-benzothioxaborine (IIa), yield 65%, bp 50-52° (3 mm); nmr (deuteriochloroform): δ 1.20 (t, 3H, CH₃, J = 7.1 Hz); 3.98 (q, 2H, CH₂CH₃, J = 7.1 Hz); 5.03 (s, 2H, CH₂) and 7.0-7.4 ppm (m, 4H aromatic).

Anal. Calcd. for C₉H₁₁BO₂S: C, 55.70; H, 5.71; B, 5.57; S, 16.52. Found: C, 55.57; H, 5.73; B, 5.60; S, 16.48.

2-Isopropoxy-4*H*-1,3,2-benzothioxaborine (IIb).

This compound was obtained with a yield of 60% by the above described method for IIa, bp 55-59° (3 mm); nmr (deuteriochloroform): δ 1.15 (d, 6H, 2CH₃, J = 6.14); 3.45 (m, 1H, CH); 4.94 (s, 2H, CH₂) and 7.11 - 7.26 ppm (m, 4H aromatic).

Anal. Calcd. for C₁₀H₁₃BO₂S: C, 57.72; H, 6.30; B, 5.19; S, 15.40. Found: C, 57.50; H, 6.32; B, 5.20; S, 15.44.

2-Phenoxy-4*H*-1,3,2-benzothioxaborine (IIc).

Method A.

This compound was obtained with a yield of 80% by the above described method for IIa, bp 68-70° (3 mm); nmr (deuteriochloroform): δ 6.05 (s, 2H, CH₂) and 6.75 - 7.30 ppm (m, 9H aromatic).

Anal. Calcd. for C₁₃H₁₁BO₂S: C, 64.49; H, 4.58; B, 4.46; S, 13.24. Found: C, 64.29; H, 4.59; B, 4.43; S, 13.20.

Method B.

A mixture of 2-isopropoxy-4*H*-1,3,2-benzothioxaborine (IIb) (0.01 mole) and phenol (0.01 mole) in benzene (40 ml) was refluxed for 4 hours. On removal of the excess of benzene under vacuum, the residue afforded on distillation the product IIc.

2-Isopropoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIa).

A mixture of isopropyl borate (0.019 mole) and 2-aminobenzyl alcohol (0.019 mole) in benzene (60 ml) was refluxed for 3 hours. On removal of the excess benzene under vacuum the residue afforded, on distillation, 2-isopropoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIa), yield 70%, bp 139-140° (20 mm); nmr (deuteriochloroform): δ 1.13 (d, 6H, 2CH₃, J = 6.1 Hz); 4.72 (m, 1H, CH); 4.98 (s, 2H, CH₂) and 6.40 - 7.40 ppm (m, 4H aromatic).

Anal. Calcd. for $C_{10}H_{14}BNO_2$: C, 62.87; H, 7.38; B, 5.65; N, 7.33. Found: C, 62.75; H, 7.36; B, 5.68; N, 7.31.

2-*n*-Butoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIb).

Method A.

This compound was obtained with a yield of 65% by the above described method for IIIa, bp 142-143° (20 mm); nmr (deuteriochloroform): δ 0.86 (t, 3H, CH_3); 1.32 - 1.47 (m, 4H, $2CH_2$); 3.72 (t, 2H, CH_2); 4.99 (s, 2H, CH_2) and 6.53 - 7.16 (m, 4H aromatic).

Anal. Calcd. for $C_{11}H_{16}BNO_2$: C, 64.42; H, 7.86; B, 5.27; N, 6.83. Found: C, 64.40; H, 7.83; B, 5.25 N, 6.81.

Method B.

A mixture of 2-isopropoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIa) (0.01 mole) and *n*-butyl alcohol (0.01 mole) in benzene (50 ml) was refluxed for 4 hours. On removal of the excess of the solvent under vacuum the residue afforded on distillation under reduced pressure the desired IIIb.

2-Phenoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIc). Method A.

This compound was obtained with a yield of 70% by the method described for IIIa, bp 135° (10 mm); nmr (deuteriochloroform): δ 5.48 (s, 2H, CH_2) and 6.68-7.12 ppm (m, 9H aromatic).

Anal. Calcd. for $C_{13}H_{12}BNO_2$: C, 69.37; H, 5.37; B, 4.80; N, 6.22. Found: C, 69.40; H, 5.35; B, 4.78; N, 6.20.

Method B.

A mixture of 2-isopropoxy-1*H*,4*H*-1,3,2-benzazoxaborine (IIIa) (0.01

mole) and phenol (0.01 mole) in benzene (50 ml) was refluxed for 4 hours. On removal of the excess of the solvent under vacuum, the residue afforded on distillation under reduced pressure the desired product IIIc.

2-Phenyl-1*H*,4*H*-1,3,2-benzazoxaborine (IV).

A solution of 2-aminobenzyl alcohol (0.01 mole) and benzene-boronic acid (0.01 mole) in 100 ml of dry benzene was heated under reflux for 3 hours, collecting the water formed in a Dean-Stark apparatus. The solvent was removed under vacuum and the residue afforded on distillation 2-phenyl-1*H*,4*H*-1,3,2-benzazoxaborine (IV), yield 60%, bp 210-215° (25 mm), mp 74-75°; nmr (deuteriochloroform): δ 5.16 (s, 2H, CH_2) and 6.87-7.38 ppm (m, 9H aromatic).

Anal. Calcd. for $C_{13}H_{12}BNO$: C, 74.68; H, 5.78; B, 5.17; N, 6.70. Found: C, 74.71; H, 5.80; B, 5.15. N, 6.68.

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