Preparation of Some 1,3,2-Benzoxathiaborole Derivatives (1)

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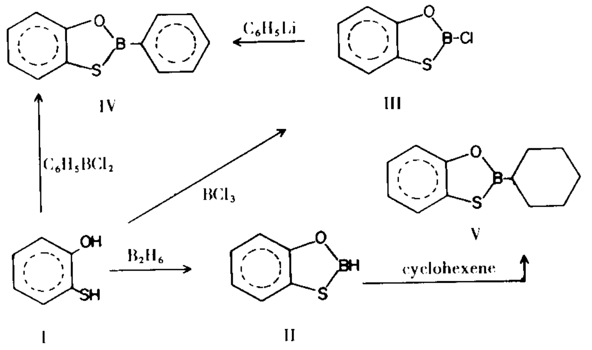
Benzo derivatives of five-membered rings which contain an O-B-S linkage have not been reported previously. In this preliminary paper, the preparation of 1,3,2-benzoxathiaborole (II) and some 2-substituted derivatives, is described. The reactions performed are shown in scheme I. Derivatives II, III, IV and V are thermally stable and can be distilled under reduced pressure; however, all spontaneously hydrolyze in the presence of moisture. The conversion of II → V indicates that 1,3,2-benzoxathiaborole (II) can be used as a hydroborating agent.



(Scheme I)

EXPERIMENTAL

Literature procedures were followed in the preparation of 2-hydroxythiophenol (2), phenyllithium (3), phenylboron dichloride (4) and diborane (5). All operations involved in the preparation, transfer and distillation of II, III, IV and V were carried out in an atmosphere of dry, oxygen-free nitrogen (6). Melting points were determined on a Tottoli apparatus and are uncorrected. The ir spectra were obtained in liquid film and in carbon tetrachloride on a Perkin Elmer 325 spectrophotometer. The nmr spectra were recorded in carbon tetrachloride on a Varian HA spectrometer, working at 100 MHz and using hexamethyldisiloxane as internal standard.

1,3,2-Benzoxathiaborole (II).

To a stirred solution of diborane in THF (100 ml., 200 mmoles), cooled to 0°, a solution of 2-hydroxythiophenol in THF (50 ml., 200 mmoles) was added during 1 hour. The reaction mixture was stirred at room temperature for almost 3 hours. Distillation at 95° (80 mm) gave compound II, yield 78%; n_D^{20} 1.5812; ir (neat): 2610, 1450, 1200, 740 cm^{-1}.

Anal. Calcd. for C_6H_5BOS: C, 52.99; H, 3.71; B, 7.96; S, 23.58. Found: C, 53.13; H, 3.58; B. 7.83; S, 23.30.

2-Chloro-1,3,2-benzoxathiaborole (III).

To a stirred solution of boron trichloride in methylene chloride (100 ml., 200 mmoles), cooled to −10°, a solution of 2-hydroxythiophenol in methylene chloride (50 ml., 150 mmoles) was added during 2 hours. The reaction mixture was slowly warmed to 0° (2 hours) and then to room temperature. Distillation at 72° (5 mm) gave compound III, yield 70%.

Anal. Calcd. for C_6H_4BClOS: C, 42.28; H, 2.37; B. 6.35; Cl, 20.80; S, 18.78. Found: C, 42.43; H, 2.25; B. 6.21; Cl, 20.74; S, 18.62.

2-Phenyl-1,3,2-benzoxathiaborole (IV).

Method A.

To a stirred solution of 2-chloro-1,3,2-benzoxathiaborole (III) in diethyl ether (120 ml., 120 mmoles) at −10°, an ethereal solution of phenyllithium (120 mmoles) was added. When the addition was completed the mixture was stirred at room temperature for 2 hours. The ethereal solution was filtered and fractionated. At 137° (2 mm) the compound IV was obtained, m.p. 80-82°, yield 45%.

Anal. Calcd. for $C_{12}H_9BOS$: C, 67.96; H, 4.28; B, 5.10; S, 15.12. Found: C, 67.85; H, 4.21; B, 4.98; S, 15.02.

Method B.

To a stirred solution of 2-hydroxythiophenol in benzene (250 ml., 200 mmoles) a solution of phenylboron dichloride (100 ml., 200 mmoles) in benzene was added dropwise and the mixture was refluxed for 6 hours. Distillation at 138° (2 mm) gave compound IV, m.p. 80-82°, yield 47%. The spectra registered for the products obtained by method A and B are identical; ir (carbon tetrachloride): 3080, 1600, 1495, 1430, 1330, 1230, 1150, 1125, 1070, 1020, 940, 750, 700 cm^{-1}; nmr (carbon tetrachloride): τ 2.80 (m, 7 H arom), 2.22 (m, 2 H arom).

2-Cyclohexyl-1,3,2-benzoxathiaborole (V).

A mixture of 1,3,2-benzoxathiaborole (II) (170 mmoles) and cyclohexene (160 mmoles) was refluxed for 3 hours. Distillation at 150° (70 mm) gave the compound V, yield 56%; n_D^{20} 1.5700; ir (neat): 3070, 3030, 2850, 2650, 2610, 1925, 1885, 1850, 1810, 1770, 1675, 1575, 925, 745, 660 cm^{-1}; nmr (carbon tetrachloride): τ 8.54 (m, 10 H, 4 CH_2 groups), 8.18 (m, 1 H, CH-CH_2-), 3.00 (m, 4 H arom).

Anal. Calcd. for $C_{12}H_{15}BOS$: C, 66.07; H, 6.93; B, 4.96; S, 14.70. Found: C, 66.19; H, 6.84; B, 4.88; S, 14.57.

Hydrolysis of Compounds II, III, IV, V.

All the compounds hydrolyzed spontaneously in the presence of moisture yielding 2-hydroxythiophenol; compound II by hydrolysis gave hydrogen and boric acid; III gave hydrochloric and boric acid; IV gave phenylboronic acid and V gave cyclohexylboronic acid.

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