

Contributions to the Chemistry of Boron. Part 160.¹ A Convenient Synthesis of Catecholatorborane and Diborane†

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Catecholatorborane is formed in high yield (> 75%) by ball milling NaBH₄ and 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) in diethyl ether in the presence of small amounts of LiCl. It also results quantitatively from the first two components in diglyme (MeOCH₂CH₂OCH₂CH₂OMe), but cannot be separated from the solvent. The reaction between NaBH₄ and catecholatorborane or the *o*-phenylene compound in diglyme can also be used to prepare diborane in high yield.

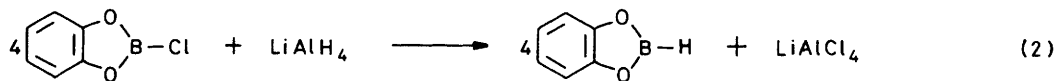
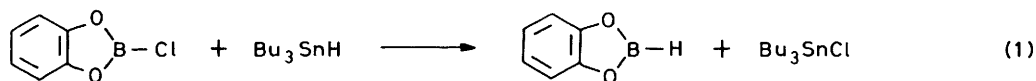
Since catecholatorborane was first used for hydroboration² considerable interest has been focused on its application as a versatile reducing agent. It reduces sulphoxides to sulphides, converts alkenes and alkynes into alkyl- or alkenyl-boronic acids, and alcohols are obtained from aldehydes, ketones, epoxides, carboxylic acids, and acid chlorides. Finally, alkanes can be prepared from alkenes and tosylhydrazones. All these reactions are well documented.³⁻⁶ In spite of this versatility, borane-dimethyl sulphide or borane-tetrahydrofuran are generally preferred over catecholatorborane as hydroborating reagents although the latter is very easy to handle and its monofunctionality allows good control of its reactions. One reason why catecholatorborane is less favoured as a reducing and hydroboration reagent may be the difficulty in isolating it in high yield. We report now a convenient synthesis for catecholatorborane which allows its isolation in yields exceeding 75%.

Results and Discussion

Catecholatorborane was first prepared in 1968 in *ca.* 42% yield by treating tributyltin hydride with 2-chloro-1,3,2-benzodioxaborole according to equation (1).⁷ Using LiAlH₄ in diethyl

to completion. However, we experienced the same difficulty as previous workers in isolating catecholatorborane from the thf solution,[‡] yields ranging from 40 to 71%. Replacement of H₃B·thf by H₃B·SMe₂ gave no improvement. At ambient temperature only a 60% conversion within 7 d was observed. This can be rationalized from the fact that the BS bond is stronger than the BO bond in these adducts, and, therefore, base displacement is more readily achieved for H₃B·thf.

In order to avoid diborane or a borane adduct in the formation of catecholatorborane the reaction of NaBH₄ with 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) was investigated. No reaction was observed in the absence of a solvent even at 250 °C. Also, the presence of benzene did not induce a reaction. However, in diethyl ether a very slow reaction to catecholatorborane was noted. In contrast, a diglyme (MeOCH₂CH₂OCH₂CH₂OMe) solution of the *o*-phenylene compound is readily reduced to catecholatorborane at ambient temperature on adding NaBH₄. Based on the stoichiometry shown in equation (5), an almost quantitative yield was obtained in the form of a diglyme solution, together with small amounts of diborane. The formation of diborane is due to reaction (6), and yields of pure diborane gas in excess of 80% are achieved.



ether according to equation (2) we arrived at a disappointing yield of 19%. This compares with a 16.7% yield of 4,4,6-trimethyl-1,3,2-dioxaborinane obtained by reducing the 2-chloro-compound with LiAlH₄.⁸ It, therefore, appears that the products formed interact with one another, making the separation of the expected hydrides very difficult.

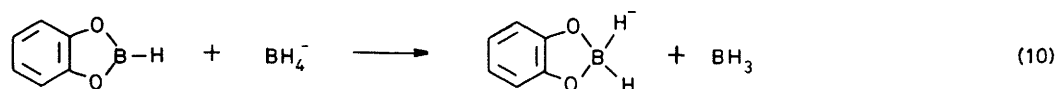
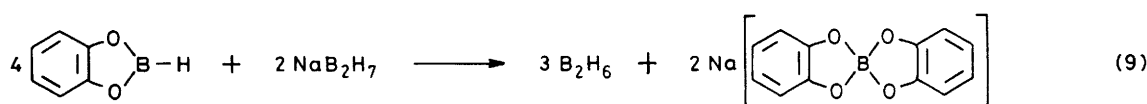
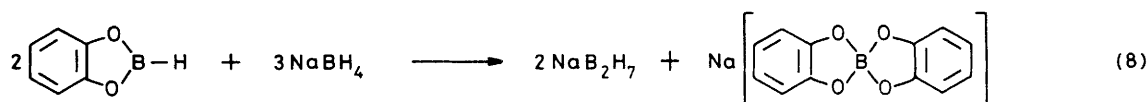
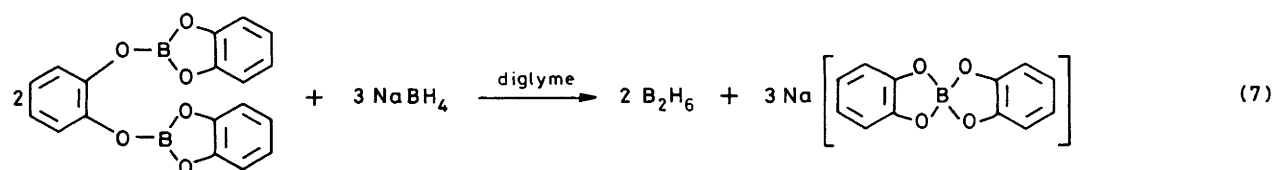
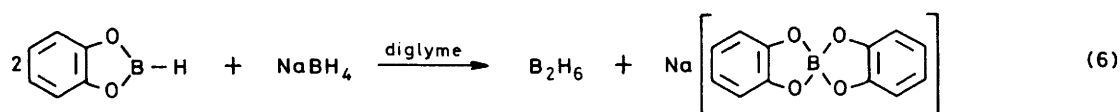
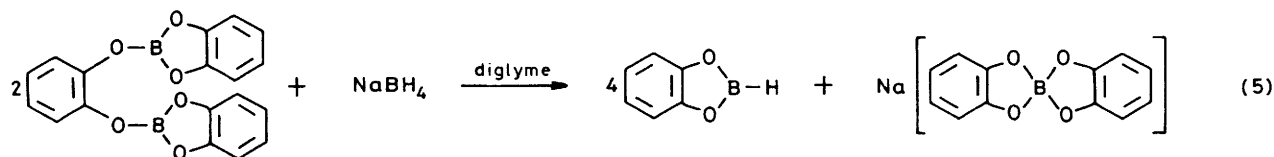
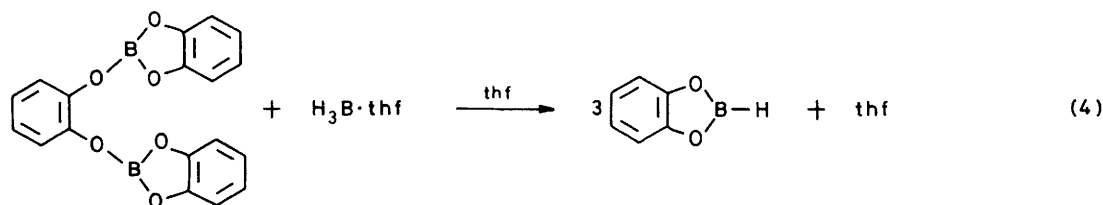
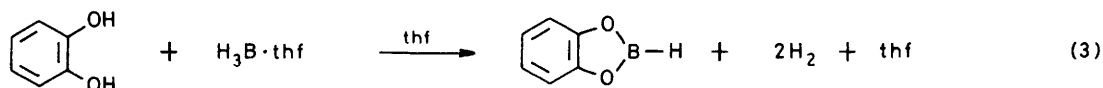
Tetrahydrofuran solutions of catecholatorborane are readily obtained by the reaction of catechol with borane in tetrahydrofuran (thf).² However, this method suffers from the disadvantage that 2 mol equivalents of hydride are lost as shown in equation (3). Also isolation of catecholatorborane from the solution in high yield presents problems. The first problem can readily be circumvented by employing the redistribution reaction (4). This reaction, though quantitative, proceeds slowly

As expected from these equations the yield of catecholatorborane increases on decreasing the ratio NaBH₄: *o*-phenylene compound while the opposite is true for diborane production. Thus, when this ratio was changed from 1:1 to 1:2 the ratio of catecholatorborane to sodium bis(catecholatorborate) changed from 51:49 to 77:23 as indicated by ¹¹B n.m.r. analysis of the solution. These experimental data compare favourably with the theoretical values of 50:50 and 80:20 respectively. Although catecholatorborane can be made conveniently according to equation (5) the problem of its isolation from the solution remains, because it co-distills with the solvent.

Diborane formed according to equation (6) or (7) can readily be separated, provided there is no excess of NaBH₄. Indeed, under the stoichiometry of equation (8) diborane remains

† Non-S.I. unit employed: mmHg ≈ 134 Pa.

‡ Literature values are: 80,² 70–80,⁴ and 50%.⁵

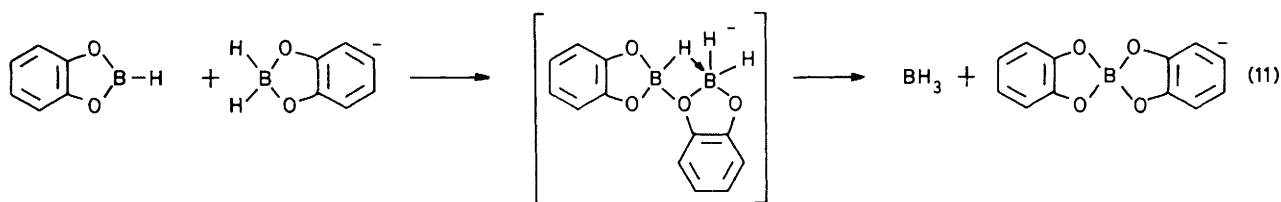


chemically bonded as sodium heptahydridoborate in solution.⁹ Reaction (8) is very fast while the diborane-releasing reaction (9) proceeds more slowly.

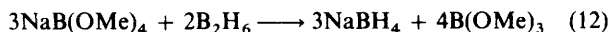
These reactions demonstrate that catecholborane and 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) are comparatively strong Lewis acids capable of hydride abstraction from NaBH₄. Therefore, the first step in the reaction of catecholborane is expected to occur according to equation (10), liberating BH₃ which can bind to NaBH₄ to produce NaB₂H₇. However, the transient existence of a catecholatodihydridoborate cannot be detected by ¹¹B n.m.r. spectroscopy. This indicates that it reacts faster with catecholborane than BH₄⁻, and equation (11) shows the attack of the Lewis acid on an oxygen atom of the catecholatodihydridoborate. The only other species that can be observed in the ¹¹B n.m.r. spectra of

the diglyme solutions besides NaBH₄ (δ -41 p.p.m., quintet), NaB₂H₇ (δ -22.7 p.p.m., q), and NaB(O₂C₆H₄)₂ (δ 14.6, s) is a very weak doublet (< 1%) at -15.3 p.p.m., which indicates the presence of a monohydridoborate species.

Analogous reactions to those reported here were not observed for B(OPh)₃ or B(OMe)₃ in diglyme at temperatures up to 200 °C.¹⁰ Only with triphenyl borate was BH₃ liberated using triethylamine as solvent and isolated in the form of Et₃N·BH₃. The higher reactivity of B(OPh)₃ as compared with B(OMe)₃ was attributed to the former being the stronger Lewis acid. This argument then stresses the fact that 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) and catecholborane are even stronger Lewis acids. Although Ashby¹⁰ did not observe a reaction of B(OMe)₃ with NaBH₄ in diglyme, there are reports that dimethoxyborane is produced by the



interaction of B(OMe)_3 or $(\text{MeO})_3\text{B}$ with NaBH_4 in polyethers.¹¹ On the other hand, the formation of NaBH_4 from NaB(OMe)_4 and diborane¹² as in equation (12) or dimethoxyborane is well known, as is the ligand-exchange reaction (13).¹²



These are reactions in the reverse sense to those described here, and under the conditions reported NaBH_4 is formed as an insoluble product, or the borate was removed. Therefore, the interaction between NaBH_4 and B(OR)_3 ¹³ on the one hand and NaB(OR)_4 and boranes B_2H_6 or $(\text{RO})_2\text{BH}$ can best be rationalized in terms of equilibria, with product formation depending strongly on the reaction conditions.

As pointed out earlier, the high-yield process (5) for catecholatorborane has the disadvantage that this product cannot be separated from the solvent. In order to overcome this problem a less basic solvent of lower boiling point was necessary in which the tetrahydridoborate was soluble to a certain extent. Diethyl ether does not fulfil this second requirement for NaBH_4 . However, it is known¹⁴ that metathesis with LiCl produces the ether-soluble LiBH_4 . Therefore, we added small amounts (5 mol %) of LiCl to a mixture of NaBH_4 and 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) according to equation (5). Ball milling in ether produced catecholatorborane in yields $\geq 78\%$. Therefore, catecholatorborane has now become a readily accessible reagent.

Experimental

All manipulations were carried out under rigorously anhydrous conditions in an oxygen-free dinitrogen atmosphere using Schlenk techniques. Solvents were carefully dried and stored under N_2 . The compounds BH_3 in tetrahydrofuran¹⁵ and $\text{H}_3\text{B}\cdot\text{SMe}_2$ ¹⁶ were prepared by literature procedures. Commercial NaBH_4 was heated under vacuum to 150°C for 2 h and ground in a steel ball mill. Freshly sublimed commercial grade catechol was used for the preparation of 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole). All reactions were monitored by ^{11}B n.m.r. spectroscopy using a Varian FT 80 or Bruker WP 200 instrument, the chemical shifts being referred to $\text{F}_3\text{B}\cdot\text{OEt}_2$ as standard.

2,2'-*o*-Phenylenedioxybis(1,3,2-benzodioxaborole).¹⁷—Catechol (189 g, 1.71 mol) and B_2O_3 (39.5 g, 0.57 mol) were allowed to react in a Dean-Stark apparatus using 200 cm^3 of benzene or toluene until the required amount of water (31 cm^3) had been collected (ca. 20 h). Most of the solvent was removed by distillation, the rest *in vacuo*. The reaction flask was then immersed in a hot bath while retaining the vacuum. At 150°C some solid sublimed within 2 h. The residue was then distilled, discarding a moderate forerun of 10 cm^3 . Yield: 185 g (93%), b.p. $176\text{--}177^\circ\text{C}$ ($7 \times 10^{-2}\text{ mmHg}$).

2-Chloro-1,3,2-benzodioxaborole.*—Liquid BCl_3 (3.85 cm^3 , 46.0 mmol) was condensed into a solution of 2,2'-*o*-phenyl-

enedioxybis(1,3,2-benzodioxaborole) in benzene (40 cm^3). The mixture was then allowed to warm to ambient temperature. After 3 h the solvent was removed at reduced pressure and the residue distilled at 50°C (1 mmHg). Yield: 20.6 g (98%).

Catecholatorborane.—(a) 2-Chloro-1,3,2-benzodioxaborole (14.19 g, 92.4 mmol), dissolved in diethyl ether (35 cm^3), was added dropwise to a stirred solution of LiAlH_4 (0.93 g, 24.5 mmol) in ether (30 cm^3) at 0°C . The mixture was stirred for 24 h at room temperature. Fractional distillation produced 2.15 g of catecholatorborane (19%), b.p. 76°C (100 mmHg).

(b) 2,2'-*o*-Phenylenedioxybis(1,3,2-benzodioxaborole) (39.75 g, 115 mmol) was stirred with $\text{H}_3\text{B}\cdot\text{SMe}_2$ (8.73 g, 115 mmol) for 12 d. Benzene (25 cm^3) was then added and the mixture stirred for 7 d. ^{11}B n.m.r. spectra indicated a ca. 60% conversion into catecholatorborane [δ 28.3 (d), 22 (s, shoulder), and -19.8 p.p.m. (q)].

(c) A 1.35 mol dm^{-3} solution of BH_3 (89 cm^3 , 120 mmol) in thf was added to 2,2'-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) (41.55 g, 120 mmol) which slowly dissolved on stirring. The reaction was complete after 30 h, as shown by a single ^{11}B n.m.r. signal at 25 p.p.m. (d). Most of the solvent was removed by adding the catecholatorborane solution dropwise into a Schlenk tube kept at $40\text{--}50\text{ mmHg}$ at ambient temperature. The concentrated solution was then distilled, yielding 30.7 g of catecholatorborane (71%), b.p. 76°C (100 mmHg).

Reactions of 2,2'-*o*-Phenylenedioxybis(1,3,2-benzodioxaborole) with Sodium Tetrahydridoborate.—(a) A mixture of the *o*-phenylene compound (10.35 g, 30 mmol) and NaBH_4 (0.57 g, 15 mmol) was slowly heated to 250°C at 100 mmHg. No catecholatorborane condensed in an attached cold-trap within 2 h.

(b) The same amounts of reactants were kept in refluxing benzene (100 cm^3) for 7 h. No reaction was noted by ^{11}B n.m.r. spectroscopy.

(c) The *o*-phenylene compound (29.17 g, 84.3 mmol), NaBH_4 (2.23 g, 58.9 mmol), and diethyl ether (150 cm^3) were kept under reflux for 110 h. All material volatile up to 80°C ($5 \times 10^{-2}\text{ mmHg}$) was then distilled from the mixture. Fractional distillation of the condensate produced 5.4 g of catecholatorborane (27%), b.p. 76°C (100 mmHg).

(d) A solution of NaBH_4 (1.29 g, 34.1 mmol) in diglyme (25 cm^3) was added to the *o*-phenylene compound (23.64 g, 68.3 mmol) in 20 cm^3 of this solvent. A slow stream of nitrogen was passed over the stirred solution, and the diborane carried away was absorbed in acetone. After stirring overnight, distillation at $80\text{--}100^\circ\text{C}$ (100 mmHg) produced 37 cm^3 of a 3.6 mol dm^{-3} catecholatorborane solution (yield 97%). The non-volatile residue was dried at 10^{-2} mmHg , 100°C , and identified as $\text{NaB(O}_2\text{C}_6\text{H}_4)_2$ by comparison of its ^{11}B n.m.r. spectrum (δ 14.6 p.p.m. in diglyme) and i.r. spectrum with those of an authentic sample prepared from catechol and NaBH_4 .¹⁸

* Previous preparations include the reaction of $\text{C}_6\text{H}_4\text{O}_2\text{SO}$ and BCl_3 (J. Charalambous, H. J. Davies, M. J. Frazer, and W. Gerrard, *J. Chem. Soc.*, 1962, 1505) or $\text{C}_6\text{H}_4(\text{OH})_2$ with BCl_3 (W. Gerrard, M. F. Lappert, and B. A. Mountfield, *J. Chem. Soc.*, 1959, 1529).

(e) The *o*-phenylene compound (185 g, 0.53 mol) and NaBH₄ (10.1 g, 0.27 mol) were allowed to react in a steel ball mill after adding diethyl ether (400 cm³) and LiCl (570 mg). After 55 h all volatiles were removed *in vacuo* directly from the mill (using a water-bath). Fractional distillation of the condensate yielded 99 g (78%) of catecholoborane, b.p. 75–76 °C (100 mmHg).

Diborane.—(a) To a solution of NaBH₄ (0.84 g, 22.2 mmol) in diglyme (15 cm³) was added dropwise with stirring under a slow stream of nitrogen gas a solution of catecholoborane (5.32 g, 44.4 mmol) in diglyme (25 cm³). Diborane was absorbed in acetone and its boron content determined after an overnight run (16 h). Yield: 86%. After evaporation of the solvent the solid residue was dried at 100 °C (10⁻² mmHg). Yield: 5.3 g NaB(O₂C₆H₄)₂ (95.5%), identified by i.r. and ¹¹B n.m.r. spectroscopy.

(b) A suspension of NaBH₄ (2.90 g, 76.6 mmol) in diglyme (10 cm³) was added to a stirred solution of 2,2'-*o*-phenylenedioxybis(1,3,2-dioxaborole) (17.64 g, 51 mmol) in the same solvent (50 cm³). The reaction flask was cooled with tap water. Dry nitrogen gas was used to drive the produced diborane slowly through traps kept at -78 and -196 °C, and diborane condensed in the latter. After 1 h the reaction mixture was heated to 90 °C for 90 min. The diborane condensed at -196 °C was passed through a trap kept at -78 °C in a high vacuum system and condensed at -196 °C. 30.0 mmol (59%) of pure diborane were obtained. Its purity was checked by measuring its vapour pressure.

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