Contributions to the Chemistry of Boron. Part 160.[1] A Convenient Synthesis of Catecholatoborane and Diborane†

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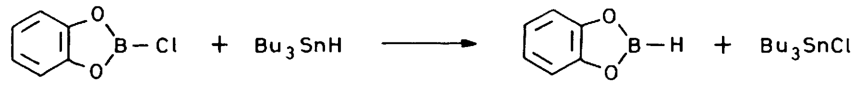
Catecholatoborane is formed in high yield (> 75%) by ball milling $NaBH_4$ and 2,2′-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) in diethyl ether in the presence of small amounts of LiCl. It also results quantitatively from the first two components in diglyme ($MeOCH_2CH_2OCH_2CH_2OMe$), but cannot be separated from the solvent. The reaction between $NaBH_4$ and catecholatoborane or the *o*-phenylene compound in diglyme can also be used to prepare diborane in high yield.

Since catecholatoborane was first used for hydroboration[2] 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 catecholatoborane as hydroborating reagents although the latter is very easy to handle and its monofunctionality allows good control of its reactions. One reason why catecholatoborane 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 catecholatoborane which allows its isolation in yields exceeding 75%.

Results and Discussion

Catecholatoborane 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 $LiAlH_4$ in diethyl 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 $LiAlH_4$.[8] It, therefore, appears that the products formed interact with one another, making the separation of the expected hydrides very difficult.



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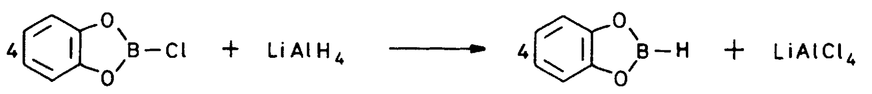

(2)

Tetrahydrofuran solutions of catecholatoborane 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 catecholatoborane 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 to completion. However, we experienced the same difficulty as previous workers in isolating catecholatoborane from the thf solution,‡ yields ranging from 40 to 71%. Replacement of H_3B·thf by $H_3B{\cdot}SMe_2$ 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 H_3B·thf.

In order to avoid diborane or a borane adduct in the formation of catecholatoborane the reaction of $NaBH_4$ 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 catecholatoborane was noted. In contrast, a diglyme ($MeOCH_2CH_2OCH_2CH_2OMe$) solution of the *o*-phenylene compound is readily reduced to catecholatoborane at ambient temperature on adding $NaBH_4$. Based on the stoicheiometry 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.

As expected from these equations the yield of catecholatoborane increases on decreasing the ratio $NaBH_4$: *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 catecholatoborane to sodium bis(catecholato)borate changed from 51:49 to 77:23 as indicated by ^{11}B n.m.r. analysis of the solution. These experimental data compare favourably with the theoretical values of 50:50 and 80:20 respectively. Although catecholatoborane can be made conveniently according to equation (5) the problem of its isolation from the solution remains, because it co-distils with the solvent.

Diborane formed according to equation (6) or (7) can readily be separated, provided there is no excess of $NaBH_4$. Indeed, under the stoicheiometry of equation (8) diborane remains

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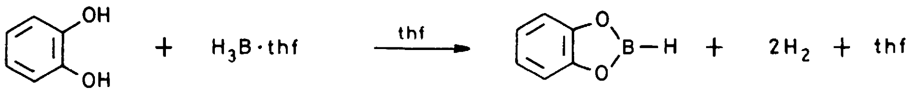
† *Non-S.I. unit employed:* mmHg ≈ 134 Pa.

‡ Literature values are: 80,[2] 70—80,[4] and 50%.[5]



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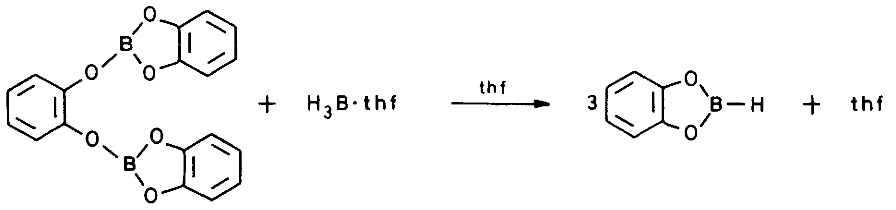

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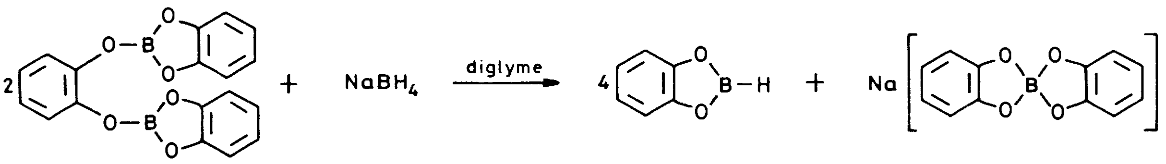

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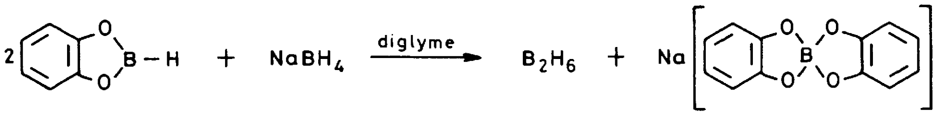

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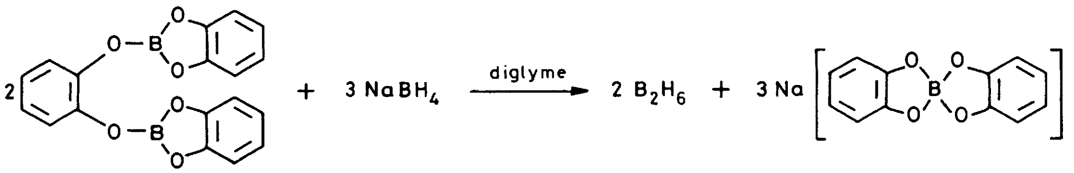

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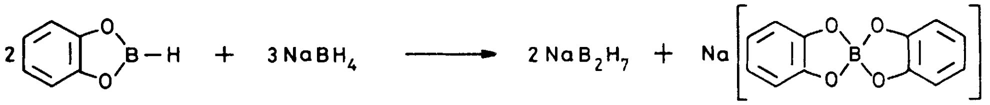

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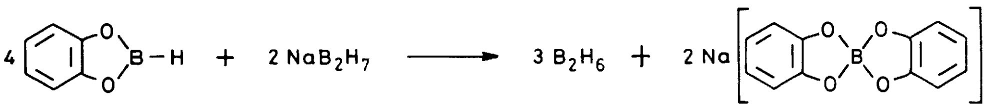

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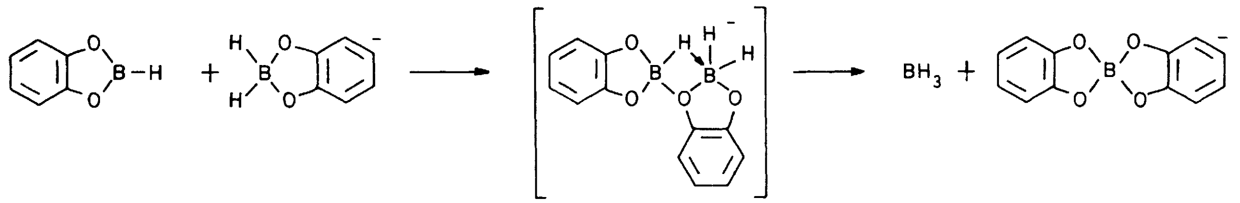
(10)

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

These reactions demonstrate that catecholatoborane and 2,2′-*o*-phenylenedioxybis(1,3,2-benzodioxaborole) are comparatively strong Lewis acids capable of hydride abstraction from $NaBH_4$. Therefore, the first step in the reaction of catecholatoborane is expected to occur according to equation (10), liberating BH_3 which can bind to $NaBH_4$ to produce NaB_2H_7. However, the transient existence of a catecholatodihydridoborate cannot be detected by ^{11}B n.m.r. spectroscopy. This indicates that it reacts faster with catecholatoborane than BH_4^-, 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 ^{11}B n.m.r. spectra of the diglyme solutions besides $NaBH_4$ (δ −41 p.p.m., quintet), NaB_2H_7 (δ −22.7 p.p.m., q), and $NaB(O_2C_6H_4)_2$ (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 BH_3 liberated using triethylamine as solvent and isolated in the form of $Et_3N{\cdot}BH_3$. 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 catecholatoborane are even stronger Lewis acids. Although Ashby[10] did not observe a reaction of $B(OMe)_3$ with $NaBH_4$ in diglyme, there are reports that dimethoxyborane is produced by the



(11)

interaction of B(OMe)$_3$ or (MeOBO)$_3$ with NaBH$_4$ in polyethers.[11] On the other hand, the formation of NaBH$_4$ from NaB(OMe)$_4$ and diborane[12] as in equation (12) or dimethoxyborane is well known, as is the ligand-exchange reaction (13).[12]

$$3NaB(OMe)_4 + 2B_2H_6 \longrightarrow 3NaBH_4 + 4B(OMe)_3 \quad (12)$$

$$4NaBH(OMe)_3 \longrightarrow NaBH_4 + 3NaB(OMe)_4 \quad (13)$$

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$_2$H$_6$ or (RO)$_2$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 catecholatoborane 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 known[14] 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 catecholatoborane in yields ≥ 78%. Therefore, catecholatoborane 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 tetrahydrofuran[15] and H$_3$B·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 F$_3$B·OEt$_2$ as standard.

2,2′-o-Phenylenedioxybis(1,3,2-*benzodioxaborole*).[17]—Catechol (189 g, 1.71 mol) and B$_2$O$_3$ (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—177 °C (7 × 10^{-2} 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*-phenylenedioxybis(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%).

Catecholatoborane.—(*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 catecholatoborane (19%), b.p. 76 °C (100 mmHg).

(*b*) 2,2′-*o*-Phenylenedioxybis(1,3,2-benzodioxaborole) (39.75 g, 115 mmol) was stirred with H$_3$B·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 catecholatoborane [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 catecholatoborane solution dropwise into a Schlenk tube kept at 40—50 mmHg at ambient temperature. The concentrated solution was then distilled, yielding 30.7 g of catecholatoborane (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 catecholatoborane 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 × 10^{-2} mmHg) was then distilled from the mixture. Fractional distillation of the condensate produced 5.4 g of catecholatoborane (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—100 °C (100 mmHg) produced 37 cm^3 of a 3.6 mol dm^{-3} catecholatoborane solution (yield 97%). The non-volatile residue was dried at 10^{-2} mmHg, 100 °C, and identified as NaB(O$_2$C$_6$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]

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* Previous preparations include the reaction of C$_6$H$_4$O$_2$SO and BCl$_3$ (J. Charalambous, H. J. Davies, M. J. Frazer, and W. Gerrard, *J. Chem. Soc.*, 1962, 1505) or C$_6$H$_4$(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 $NaBH_4$ (10.1 g, 0.27 mol) were allowed to react in a steel ball mill after adding diethyl ether (400 cm^3) 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 catecholatoborane, b.p. 75—76 °C (100 mmHg).

Diborane.—(*a*) To a solution of $NaBH_4$ (0.84 g, 22.2 mmol) in diglyme (15 cm^3) was added dropwise with stirring under a slow stream of nitrogen gas a solution of catecholatoborane (5.32 g, 44.4 mmol) in diglyme (25 cm^3). 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 $NaB(O_2C_6H_4)_2$ (95.5%), identified by i.r. and ^{11}B n.m.r. spectroscopy.

(*b*) A suspension of $NaBH_4$ (2.90 g, 76.6 mmol) in diglyme (10 cm^3) 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 cm^3). 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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