787. *Organic Derivatives of Boron. Part II.*[1] *Catechol Derivatives.*

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Ethyl *o*-phenylene borate and tri-*o*-phenylene bisborate have been prepared by azeotropic distillation of catechol with various proportions of ethyl borate in benzene. They are interconvertible. From the former several other alkyl derivatives have been obtained, again by azeotropic distillation. The esters give amine adducts except when internal co-ordination intervenes.

GERRARD, LAPPERT, and MOUNTFIELD [2] recently prepared some catechol borate esters by treating boron trichloride with catechol or *o*-phenylene chloroboronate with other alcohols and amines. We have prepared borate esters from catechol and ethyl borate by the azeotropic distillation technique which we used earlier for alkoxides of various metals.[3]

The reaction of ethyl borate with catechol in 1 : 1 or 2 : 1 molar ratio yielded ethanol

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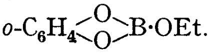
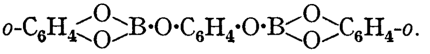
[1] Part I, Mehrotra and Strivastava, *J. Indian Chem. Soc.*, 1961, **38**, 1.

[2] Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.

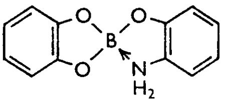
[3] Verma and Mehrotra, *J. prakt. Chem.*, 1959, **8**, 64, 235; *J.*, 1960, 2966; Kapoor and Mehrotra, *Z. anorg. Chem.*, 1957, **293**, 92, 100; *J. Amer. Chem. Soc.*, 1958, **80**, 3569; 1960, **82**, 3495; Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585; 1954, **31**, 85.

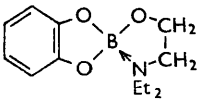
(which was removed azeotropically with benzene) and ethyl *o*-phenylene borate  $o\text{-}C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}B\cdot OEt$. Using a 2 : 3 or 1 : 4 molar ratio yielded tri-*o*-phenylene bisborate  $o\text{-}C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}B\cdot O\cdot C_6H_4\cdot O\cdot B{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_4\text{-}o$. When refluxed with 1 mol. of ethyl borate this afforded ethyl *o*-phenylene borate quantitatively.

By transesterification, the ethoxy-group of ethyl *o*-phenylene borate was replaced by higher alkoxy-groups and a number of new alkyl *o*-phenylene borates were thus prepared. These included the t-butyl and t-pentyl esters, showing the advantage of the azeotropic distillation technique, since these esters cannot be prepared from *o*-phenylene chloroboronate by the action of tertiary alcohols because of a side reaction between hydrogen chloride and the alcohol.

Alkyl *o*-phenylene borates are colourless unimolecular liquids which are hydrolysed readily and completely to catechol and boric acid. Only a few such esters have previously been prepared.[2,4] Pyridine and aniline complexes were at once precipitated on admixture of the components in benzene; tri-*o*-phenylene bisborate gave a stable 1 : 2 complex.

Ethyl *o*-phenylene borate with *o*-aminophenol or diethylaminoethanol gave the esters (I) and (II); these do not give addition complexes with amines owing to internal co-ordination as shown.

(I) 

 (II)

EXPERIMENTAL

The methods used were those already described.[1] Molecular weights were determined by a semimicro-ebulliometer (Gallenkamp) with thermistor sensing.

Ethyl o-*Phenylene Borate.*—Ethyl *o*-phenylene borate was obtained by the refluxing of ethyl borate with catechol in benzene for 2—3 hr. Ethanol produced was removed azeotropically and the compound was distilled. It had b. p. 86°/8 mm. (Found: B, 6·45; EtO, 26·9%; *M*, 160. Calc. for $C_8H_9BO_3$: B, 6·6; EtO, 27·4%; *M*, 164).

Catechol [(i) 5·85 g.; (ii) 3·58 g.] with ethyl borate [(i) 7·76 g., 1 mol.; (ii) 9·52 g., 2 mol.] in refluxing benzene (40 g.) yielded ethanol (1·9 mol.) and ethyl *o*-phenylene borate [(i) 6·6 g., 80%; (ii) 5·3 g.].

Tri-*o*-phenylene bisborate (11·65 g., 1 mol.) was refluxed for 6 hr. with ethyl borate (4·92 g., 1 mol.) in benzene (15 g.). After removal of the benzene, ethyl *o*-phenylene borate (13·6 g., 83%) was obtained at 92°/10·5 mm.

*Tri-*o-*phenylene Bisborate.*—(*a*) Fractionation of a mixture of catechol [(i) 8·25 g., 1·5 mol.; (ii) 12·66 g., 4 mol.] and ethyl borate [1 mol. (i) 7·3 g.; (ii) 4·20 g.] in benzene (40 g.) yielded the alcohol–benzene azeotrope and then tri-*o*-phenylene bisborate (7·5 g., 87%; m. p. 104°) at 214°/4 mm. (Found: B, 6·2; $C_6H_4O_2$, 92·5%; *M*, 340. Calc. for $C_{18}H_{12}B_2O_6$: B, 6·3; $C_6H_4O_2$, 93·6%; *M*, 346).

(*b*) Catechol (2·2 g., 1 mol.) and ethyl *o*-phenylene borate (6·5 g., 2 mol.) in benzene (40 g.), on fractionation, gave ethanol (1·7 g., 1·9 mol.) and then tri-*o*-phenylene bisborate (6·2 g., 90%) at 214—216°/4 mm.

Alkyl o-*Phenylene Borates.*—These were prepared by alcohol interchange in benzene. For example, propan-2-ol (2·05 g.) was added to ethyl *o*-phenylene borate (4·45 g.) in benzene (35 g.). The mixture was refluxed for 2 hr. and then slowly fractionated. Ethanol was obtained in the azeotrope. After removal of benzene, the compound was distilled. The Table gives details for these products.

o-*Aminophenyl* o-*Phenylene Borate.*—Fractionation of a mixture of *o*-aminophenol (4 g.) and ethyl *o*-phenylene borate (6·03 g.) in benzene (40 g.) gave ethanol (1·5 g., 0·9 mol.) and o-*aminophenyl* o-*phenylene borate* which was purified by sublimation at 270—290°/2 mm. (yield 6 g.; m. p. 280°) (Found: B, 4·6; N, 6·1.. $C_{12}H_{10}BNO_3$ requires B, 4·7; N, 6·1%).

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[4] Thomas, *J.*, 1946, 820, 823.

Alkyl o-*phenylene borates.*

Ester	Ethanol (%) found in the azeotrope	Yield (%) of distilled compound	B. p. (°/mm.) of the ester	B (%) Found	B (%) Reqd.
Pr^i	85	67	62/1·5	6·0	6·1
Bu^t	94	90	85/3	5·5	5·6
$CHMePr^n$	98	98	97/2·5	5·2	5·3
CMe_2Et	90	74	96/4·5	5·1	5·3
Allyl	89	82	93/4·5	6·0	6·1

2-Diethylaminoethyl o-*Phenylene Borate.*—2-Diethylaminoethanol (3·78 g.) was added to ethyl *o*-phenylene borate (5·14 g.) in benzene (40 g.). Heat was evolved and an addition compound separated. After 3 hours' refluxing, the benzene–ethanol azeotrope was slowly removed (ethanol, 1·3 g., 0·9 mol.) and *2-diethylaminoethyl* o-*phenylene borate*, m. p. 115°, was obtained (Found: B, 6·0; N, 5·7. $C_{12}H_{18}BNO_3$ requires B, 6·1; N, 5·9%).

Pyridine Complexes.—*Bispyridine tri*-o-*phenylene bisborate adduct* (1·15 g., 91%), m. p. 155—160° (Found: B, 4·1. $C_{28}H_{22}B_2N_2O_6$ requires B, 4·3%), was obtained from the base (0·4 g., 2 mol.) on admixture with tri-*o*-phenylene bisborate (0·87 g., 1 mol.) in benzene and filtration of the precipitate.

Pyridine–o-*phenylene t-butyl borate adduct* (1·2 g., 90%), m. p. 143—145° (Found: B, 4·0. $C_{15}H_{18}BNO_3$ requires B, 4·0%), was similarly obtained by adding pyridine (0·4 g., 1 mol.) to the ester (0·96 g., 1 mol.) in benzene.

Aniline Complexes.—*Aniline complexes* were prepared in the same way as the pyridine complexes. The essential details are tabulated.

Aniline complex	M. p.	B (%) Found	B (%) Reqd.	N (%) Found	N (%) Reqd.
$(C_6H_4O_2)_3B_2,2C_6H_5{\cdot}NH_2$	220—225°	4·0	4·0	5·1	5·2
$C_6H_4O_2B{\cdot}O{\cdot}C_2H_5,C_6H_5{\cdot}NH_2$	215—217	4·2	4·2	5·3	5·4
$C_6H_4O_2B{\cdot}O{\cdot}C_3H_7,C_6H_5{\cdot}NH_2$ [a]	220—221	4·0	4·0	5·0	5·1
$C_6H_4O_2B{\cdot}O{\cdot}C_4H_9,C_6H_5NH_2$ [b]	210—212	3·8	3·8	4·8	4·9
$C_6H_4O_2B{\cdot}O{\cdot}C_5H_{11},C_6H_5{\cdot}NH_2$ [c]	222—223	3·5	3·6	4·5	4·7
$C_6H_4O_2B{\cdot}O{\cdot}C_5H_{11},C_6H_5{\cdot}NH_2$ [d]	242—244	3·6	3·6	4·5	4·7
$C_6H_4O_2B{\cdot}O{\cdot}C_3H_5,C_6H_5NH_2$ [e]	232—233	3·9	4·0	5·0	5·2

[a] Isopropyl. [b] t-Butyl. [c] s-pentyl. [d] t-Pentyl. [e] Allyl.

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