193. *Organic Derivatives of Boron. Part IV.*[1] *2-Methylpentane-2,4-diol Derivatives.*

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Reactions between ethyl borate and 2-methylpentane-2,4-diol in different stoicheiometric ratios have been carried out. A number of alkyl 1,1,3-trimethyltrimethylene borates have been prepared by transesterification between the ethyl member and higher alcohols. 1,1,3-Trimethyltrimethylene hydrogen borate, bis-(1,1,3-trimethyltrimethylene) pyroborate, and three alkylene bis-(1,1,3-trimethyltrimethylene borates) have also been synthesised.

VARIOUS stable mixed cyclic orthoborates have recently been prepared from catechol [2,3] and ethylene,[4,5] propylene, and trimethylene [1] glycol. The present paper reports the syntheses of the 2-methylpentane-2,4-diol (" hexylene glycol ") derivatives (I—IV).

Azeotropic distillation of ethyl borate and 2-methylpentane-2,4-diol in 1 : 1 or 2 : 1 molar ratio yielded ethanol and the liquid, neutral, cyclic borate (I; X = Et). Reaction with a 2 : 3 molar ratio gave the complex bisborate (III).

The ethoxy-group of the ester (I; R = Et) can be replaced by higher alkoxy-groups by alcoholysis and thus analogous alkyl esters (I; X = R) were prepared by treating the ethyl ester with a number of alcohols and phenol. The butyl ester (I; R = Bu^n) has also been prepared by treating tributyl borate with 1 mol. of 2-methylpentane-2,4-diol. Alternatively, the borates (I) are prepared by refluxing an equimolar mixture of the diol, boric acid, and alcohol and removing the water formed, azeotropically with benzene or the alcohol itself. All these compounds are colourless unimolecular liquids which are readily hydrolysed in air.

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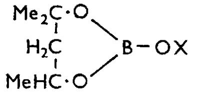
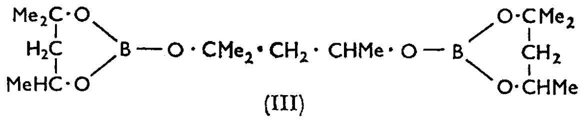
[1] Part III, Mehrotra and Srivastava, *J. Indian Chem. Soc.*, in the press.
[2] Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.
[3] Mehrotra and Srivastava, *J.*, 1961, 4045.
[4] Thomas, *J.*, 1946, 820, 823.
[5] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.

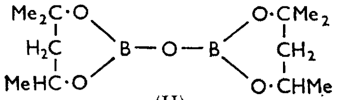
The acid ester (I; X = H), a crystalline compound, was prepared by refluxing an equimolar mixture of boric acid and 2-methylpentane-2,4-diol, the water formed being distilled off slowly. If, however, the water is removed azeotropically with benzene, the colourless liquid pyroborate (II) is obtained. This pyroborate is also obtained on distilling the acid ester under reduced pressure. It is converted into alkyl 1,1,3-trimethyltrimethylene borates (I) by refluxing with alcohols, water being removed azeotropically. The pyroborate, when exposed to air, is slowly hydrolysed to the acid ester (I; R = H); however, in presence of an excess of water, it is completely hydrolysed. The acid ester (I; R = H) is an example of the uncommon acid esters of boron, other examples being ethylene [5] and *o*-phenylene hydrogen borate.[2]



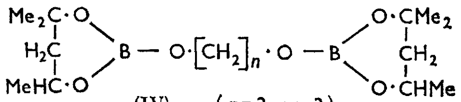
(I : X = H or R)



(III)



(II)



(IV) (n=2 or 3)

The reaction between the ester (I; R = Et) and ethylene glycol in equimolar ratio yielded 2-hydroxyethyl 1,1,3-trimethyltrimethylene borate (I; X = $O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$). On distillation, this decomposes to give ethylene bis-(1,1,3-trimethyltrimethylene borate) (IV; $n = 2$), a white solid, which was also obtained by treating the ester (I; R = Et) with ethylene glycol in 2 : 1 molar ratio. Similarly, the trimethylene diester (IV; $n = 3$) was prepared from trimethylene glycol.

EXPERIMENTAL

Preparation and Procedures.—Analytical procedures and methods for drying the reagents have been described before.[6] 2-Methylpentane-2,4-diol was distilled before use. Ethyl borate was prepared from boron trichloride and ethanol. Molecular weights were determined ebullioscopically in a semimicro-ebulliometer in carbon tetrachloride. M. p.s were determined in sealed capillary tubes.

Ethyl 1,1,3-*Trimethyltrimethylene Borate* (I; R = Et).—Fractionation of a mixture of ethyl borate [(i) 6·4 g., 1 mol.; (ii) 8·0 g., 2 mol.] and 2-methylpentane-2,4-diol [(i) 5·15 g., 1 mol.; (ii) 3·23 g.] in benzene (40 g.), after 2 hours' refluxing, yielded ethanol [(i) 3·8 g., 1·9 mol.; (ii) 2·49 g., 2 mol.] in the azeotrope and then the *ester* (I; R = Et) [(i) 6·5 g., 87%; (ii) 3·23 g., 75%] at 70°/9 mm. (Found: C, 54·1; H, 9·8; B, 6·3; EtO, 25·5%; *M*, 170. $C_8H_{17}BO_3$ requires C, 55·8; H, 9·9; B, 6·3; EtO, 26·1%; *M*, 172).

1,1,3-*Trimethyltrimethylene Bis*-(1,1,3-*trimethyltrimethylene Borate*) (III).—Ethyl borate (6·55 g., 2 mol.), 2-methylpentane-2,4-diol (7·77 g., 3 mol.), and benzene (40 g.), on being refluxed for 2 hr. and then fractionated, yielded ethanol (5·8 g., 93%) in the azeotrope and the *product* (III) (7 g., 88%), b. p. 150°/2 mm. (Found: C, 58·0; H, 9·6; B, 5·8%; *M*, 365. $C_{18}H_{36}B_2O_6$ requires C, 58·4; H, 9·7; B, 5·8%; *M*, 370).

Alkyl 1,1,3-*Trimethyltrimethylene Borates.*—These were prepared by alcohol interchange in benzene. For example, propan-2-ol (4 g.) was refluxed for 2 hr. with the ethyl ester (I; R = Et) (5·55 g.) in benzene (40 g.), then slow fractionation yielded ethanol (1·3 g., 88%) in the azeotrope. After removal of the excess of benzene, the *product* was distilled. Details are given in the Table.

The butyl ester (I; R = Bu^n) was prepared also as follows: (*a*) The diol (9·18 g., 1 mol.), boric acid (4·82 g., 1 mol.) and butan-1-ol (35 g.) were refluxed for 2 hr. and then fractionated. After removal of the water–butanol azeotrope, the excess of butanol was removed and the residue distilled; the product (14 g.) was obtained at 80°/3·5 mm. (Found: B, 5·4%). (*b*) A

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[6] Mehrotra and Srivastava, *J. Indian Chem. Soc.*, 1961, **38**, 1.

Alkyl 1,1,3-trimethyltrimethylene borates.

Alkyl	EtOH (%) in azeotrope	Yield (%) of distilled product	B. p./mm.	Found (%)			Required (%)		
				C	H	B	C	H	B
Pr^i	88	88	47°/0·6	57·8	10·1	5·8	58·0	10·2	5·8
Bu^n	91	90	79°/3·5	59·7	10·4	5·4	60·0	10·5	5·4
Bu^s	95	92	71°/3·5	59·8	10·4	5·35	59·8	10·4	5·35
Bu^t	96	88	65°/3·5	59·8	10·5	5·48	59·8	10·5	5·48
n-Pentyl	94	94	78°/0·8	61·5	10·6	5·1	61·7	10·7	5·1
$CHMePr^n$	95	93	63°/0·6	61·7	10·6	5·05	61·7	10·6	5·05
CMe_2Et	96	89	65°/2	61·6	10·7	5·1	61·6	10·7	5·1
$C_6H_{11}{\cdot}CHMe$	93	94	116°/3	65·5	11·2	4·2	65·6	11·3	4·2
Cyclohexyl	93	92	98°/1	63·5	10·0	4·8	63·7	10·2	4·8
Ph	97	95	102°/0·8	65·1	7·6	4·8	65·5	7·7	4·9
Allyl	89	82	52°/0·6	58·5	9·2	5·8	58·7	9·2	5·9
$NH_2{\cdot}CH_2{\cdot}CH_2$	95	85	140°/1 M. p. 52°	51·0	9·5	5·7	51·3	9·6	5·8

mixture of the diol (2·36 g., 1 mol.) and butyl borate (4·60 g., 1 mol.) was refluxed for 3 hr., then distilled slowly, to give butanol (2·8 g., 1·9 mol.) at 116—118° and the product (I; R = Bu^n) (3·5 g., 88%) at 80—82°/3·5 mm. (Found: B, 5·4%).

n-Propyl 1,1,3-*trimethyltrimethylene borate* (4·4 g.), b. p. 58°/0·9 mm., was obtained by heating a mixture of the pyroborate (II) (3·78 g.) and propanol (25 g.) under reflux, followed by slow fractionation (Found: C, 57·8; H, 10·1; B, 5·75. $C_9H_{19}BO_3$ requires C, 58·0; H, 10·2; B, 5·8%).

Bis-(1,1,3-*trimethyltrimethylene*) *Pyroborate*.—(*a*) 2-Methylpentane-2,4-diol (14·80 g., 1 mol.) and boric acid (7·77 g., 1 mol.) were heated at 140—160° for 4 hr. Water was distilled off slowly. 1,1,3-*Trimethyltrimethylene hydrogen borate* (18 g., 100%), m. p. 78°, was obtained as a crystalline residue (Found: C, 49·8; H, 8·9; B, 7·5. $C_6H_{13}BO_3$ requires C, 50·0; H, 9·0; B, 7·6%). On distillation it gave the *pyroborate* (III), b. p. 120°/1·5 mm. (Found: C, 53·1; H, 8·1; B, 8·1%; *M*, 272. $C_{12}H_{24}B_2O_5$ requires C, 53·3; H, 8·9; B, 8·0%; *M*, 270).

(*b*) The diol (7·12 g., 1 mol.), boric acid (3·74 g., 1 mol.), and benzene (50 g.) were refluxed for 3 hr. and fractionated. After removal of the water–benzene azeotrope and the excess of benzene, the residue was kept at 38°/0·5 mm. for 2 hr. A colourless liquid (8·12 g.) (Found: B, 7·9%) was obtained. On distillation of this the pure pyroborate was obtained at 122°/2 mm. (Found: B, 8·0%).

The pyroborate (3·5 g.) was left on a watch-glass for 4 hr. It changed into the acid ester (I; R = H) (3·7 g.), m. p. 78° (Found: B, 7·65%). After 10 days, the sample gave the same analysis, showing absence of further hydrolysis.

Reactions between the Ester (I; R = Et) *and Ethylene Glycol*.—(*a*) Ethylene glycol (1·66 g., 1 mol.) was refluxed with the ethyl ester (I; R = Et) (4·61 g., 1 mol.) in benzene (30 g.) for 1 hr. Fractionation then yielded ethanol (1·1 g., 99%) in the azeotrope. After removal of the excess of benzene and drying of the product for 3 hr. at 35°/1 mm., 2-*hydroxyethyl* 1,1,3-*trimethyltrimethylene borate* (4·98 g., 100%) was obtained (Found: C, 50·0; H, 9·1; B, 5·8. $C_8H_{17}BO_4$ requires C, 51·1; H, 9·0; B, 5·75%). On distillation of this, a few drops were obtained at 60—63°/0·1 mm. (Found: B, 1·4%) and *ethylene bis*-(1,1,3-*trimethyltrimethylene borate*) was obtained at 124°/0·1 mm.; this had m. p. 53° (Found: C, 53·2; H, 8·8; B, 6·9. $C_{14}H_{28}B_2O_6$ requires C, 53·5; H, 8·9; B, 6·9%).

(*b*) Fractionation of a mixture of the ester (I; R = Et) (5·58 g., 2 mol.) and ethylene glycol (1·01 g., 1 mol.) in benzene (40 g.) yielded ethanol (1·31 g., 89%) in the azeotrope and the ester (IV; *n* = 2) (4·9 g., 96%), m. p. 53°; b. p. 124°/0·1 mm. (Found: C, 53·3; H, 8·9; B, 6·9%).

Reaction between the Ethyl Ester (I; R = Et) *and Trimethylene Glycol*.—The ester (1·94 g., 2 mol.) and the glycol (0·43 g., 1 mol.) in benzene (30 g.) were refluxed for 2 hr. Fractionation afforded ethanol (0·5 g., 96%) and *trimethylene bis*-(1,1,3-*trimethyltrimethylene borate*) (1·9 g.), b. p. 136—139°/0·2 mm. (Found: C, 54·7; H, 9·0; B, 6·6. $C_{15}H_{30}B_2O_6$ requires C, 54·9; H, 9·1; B, 6·6%).

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