

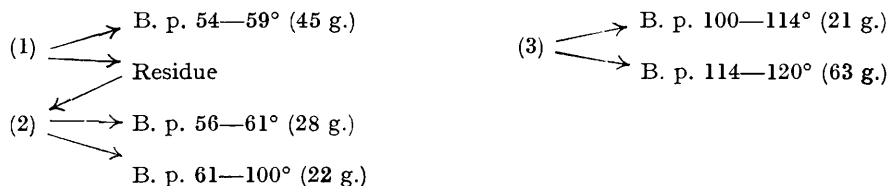
## 177. The Preparation of Mixed Organic Orthoborates.

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The preparation and properties of a number of mixed organic orthoborates are described. They have been found to "disproportionate" with great readiness.


SCHIFF (*Annalen*, Suppl., 1867, 5, 183) claimed to have prepared diethyl amyl and ethyl diamyl borates by heating together either monoethyl borate with amyl alcohol or amyl borate with ethyl borate, and to have obtained methyl diethyl borate by heating monomethyl borate with ethyl alcohol. Similar experiments have now been carried out, the following being typical.

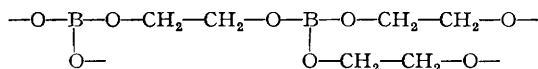
A mixture of *n*-propyl alcohol and *n*-amyl alcohol (3 g.-mols. of each) was converted into 240 c.c. of mixed borates by refluxing with benzene and boric anhydride under the conditions of Method (1) (preceding paper). The mixture so obtained was carefully fractionated under 16 mm. through a two-foot Hempel column into the following fractions: (1) 90—103°, 76 c.c.; (2) 103—135°, 48 c.c.; (3) 135—150°, 102 c.c. Each of these fractions was then separately distilled under the same conditions, but at 5 mm. The results are shown schematically below:



Fractions of b. p. 54—61°/5 mm. and 100—120°/5 mm. were found by distillation at ordinary pressure to be almost pure tri-*n*-propyl and -*n*-amyl borate, respectively. The middle fraction, b. p. 61—100°/5 mm., on redistillation under 5 mm. gave: (a) b. p. 70—100° (11 g.), (b) b. p. 100—115° (26 g.). It can be seen therefore that, although the middle fractions are persistent, their weight steadily becomes less during efforts to isolate the pure mixed borates.

A similar experiment with phenol and *n*-propyl alcohol (3 g.-mols. of each) gave 35 g. of propyl borate, b. p. 80°/18 mm., and 35 g. of phenyl borate, b. p. 190—205°/6 mm., only a few c.c. of intermediate product being obtained. It seems likely, therefore, that two simple borates B(OR)<sub>3</sub> and B(OR')<sub>3</sub> interact rapidly to give a mixture of all four possible compounds, *viz.*, these two and B(OR)(OR')<sub>2</sub> and B(OR)<sub>2</sub>(OR'). Clearly, the possibility of isolating a pure mixed borate depends on the speed with which it is rearranged on distillation; *e.g.*, B(OR)(OR')<sub>2</sub> → B(OR')<sub>3</sub> + B(OR)<sub>3</sub> + B(OR)<sub>2</sub>(OR'), and hence Schiff's claim to have isolated pure mixed borates rested on fortuitous analysis of the appropriate distillation cuts.

The mixed borates of the type considered above have, of necessity, b. p.'s intermediate between those of the corresponding simple borates, but on substitution of a suitable dihydroxy-compound in place of a monohydric alcohol, this would no longer be true. With catechol and *cyclohexyl* alcohol, for example, the following mixed borates are possible: B(C<sub>6</sub>H<sub>11</sub>O)<sub>3</sub>, B<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>3</sub>, and C<sub>6</sub>H<sub>11</sub>O-B  C<sub>6</sub>H<sub>4</sub>. Because of its much lower molecular weight, the mixed borate would possess the lowest b. p., and it should be possible to distil it out from the equilibrium mixture as it is being formed. This proved to be the case, and a number of such mixed borates have been prepared in pure condition. It must be presumed, however, that the mixed borates so obtained more or less rapidly revert to the equilibrium mixture of composition dependent on the prevailing temperature. This conclusion is supported by the fact that *cyclohexyl ethylene borate*, b. p. 119°/10 mm., a mobile liquid, on cooling sets to a glassy, almost non-flowing solid. It could not be induced to crystallize. The plastic nature of the borate is probably due to the formation of long chains as a result of this interconversion:



Those borates prepared from 1 : 2-glycols are glassy solids (Dupire, *Compt. rend.*, 1936, 202, 2096). *cyclohexyl o-phenylene borate*, on the other hand, is a crystalline solid, for the phenylene borate formed on rearrangement is a crystalline solid.

Radical interchange has been observed in the case of alkyl orthoformates by Post and Erickson (*J. Amer. Chem. Soc.*, 1933, 55, 3851), who, by the action of 1 equiv. of chloroform on 1.5 equivs. each of two aliphatic alcohols, obtained the mixed orthoformates. Here the speed of disproportionation was such that the mixed esters could be separated by fractional distillation. On standing for one month, a mixture of tri-*n*-propyl and triisooamyl orthoformate gave rise to the mixed orthoformates.

The high speed with which the mixed borates disproportionate might be considered to place the reaction in the category of tautomerism.

## EXPERIMENTAL.

*Phenyl o-Phenylene Borate*,  $C_6H_5 \cdot O \cdot B \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} C_6H_4$ .—An equimolecular mixture of 17.5 g. of boric anhydride, 47 g. of phenol, and 55 g. of catechol was made up in 300 c.c. of toluene. The water formed in the reaction was removed by co-distillation with the toluene. 150 C.c. of toluene were distilled off through a column, separated from the water, and returned to the reaction vessel. After 5 such distillations, 14.5 g. of water had been eliminated from the reaction mixture. The residue on fractionation under reduced pressure, gave 64 g. of *phenyl o-phenylene borate*, b. p. 166–167°/12 mm., the temperature then rising sharply. The mixed borate solidified on cooling to a white crystalline mass, m. p. 40–44° (yield 60%) (Found : B, 5.12.  $C_{12}H_{10}O_3B$  requires B, 5.10%).

*cycloHexyl Ethylene Borate*,  $C_6H_{11} \cdot O \cdot B \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} C_2H_4$ .—An equimolecular mixture of 17.5 g. boron oxide, 50 g. of *cyclohexanol*, and 31 g. of ethylene glycol (1 mol.) in 200 c.c. of toluene was distilled, and the condensed vapours allowed to percolate through 40 g. of anhydrous copper sulphate (see preceding paper). At the end of 5 hours, the temperature of the vapours had become constant at 110°. After removal of the toluene by distillation at ordinary pressure, the reaction product was fractionated in a vacuum through an eight-pear column. A small quantity distilled at 78–82°/14 mm., after which the temperature rose sharply to 119°/10 mm., where 51 g. (60%) of *cyclohexyl ethylene borate* were collected (Found : B, 6.30.  $C_8H_{15}O_3B$  requires B, 6.32%).

Great difficulty was experienced in collecting the mixed borate, because it set to a non-flowing, transparent, colourless, glassy mass on the cooler parts of the receiver and the column side arm; a condenser could not be employed. The difficulty was minimised by using as receiver a distillation flask with a wide side tube carrying a bottle (see Fig.). The first distillate was allowed to collect in the bulb of the receiver, the borate being then collected in the bottle by turning the flask into the correct position. The vapours were condensed, after the first few c.c. of the borate had collected, by wrapping a wet cloth around the side arm of the column. This procedure was just sufficient to condense the mixed borate to a warm liquid not too viscous to flow into the bottle.

*cycloHexyl o-Phenylene Borate*.—This was similarly prepared from 9 g. of boron oxide, 25 g. of *cyclohexanol*, and 27.5 g. of catechol, 30 g. of anhydrous copper sulphate and 150 c.c. of benzene being used. At the end of 6 hours, the temperature had become constant at 80°. The benzene was removed at ordinary pressure, and the residue fractionated

in a vacuum. A small quantity distilled at 75–120°/20 mm., and sharp separations were obtained of the mixed borate (24 g., b. p. 168°/20 mm.) and phenylene borate (12 g., b. p. 252°/14 mm.). The mixed borate set to a white mass of crystals, m. p. 55–59° (yield 44%) (Found : B, 4.91.  $C_{12}H_{15}O_3B$  requires B, 4.96%).

*n-Amyl Ethylene Borate*.—This was prepared in the same way as the *cyclohexyl ethylene ester* (12 g. of boric anhydride, 29 g. of *n-amyl alcohol*, 21 g. of ethylene glycol, 150 c.c. of toluene, 35 g. of copper sulphate). The temperature became constant at 110° after 6 hours' refluxing. The toluene was distilled off through an eight-pear column, and the residue fractionated in a vacuum: 10 c.c. came over at 70–90°/18 mm., after which the temperature rose sharply, and 28 g. of the mixed borate were collected at 108–110°/14 mm. The sample was somewhat impure (Found : B, 6.70, 6.72.  $C_7H_{15}O_3B$  requires B, 6.84%); on redistillation, 16 g., b. p. 106°/12 mm. (Found : B, 6.80%), were obtained. On cooling, it set to an extremely viscous colourless liquid.

*Phenyl Ethylene Borate*.—17.5 G. of boron oxide, 47 g. of phenol, 31 g. of ethylene glycol, and 200 c.c. of benzene were refluxed for 7 hours in the usual way through 40 g. of anhydrous copper sulphate. The product was distilled at ordinary pressure, and the mixed borate collected at 250–268°. Redistillation gave 40 g., b. p. 262–268°. As analysis showed the sample to be impure, it was redistilled under reduced pressure; 12 g. were collected, b. p. 123–127°/5 mm. On cooling, it set to a transparent, colourless, glassy solid (Found : B, 6.78.  $C_8H_9O_3B$  requires B, 7.07%).

The phenol was determined by titration with potassium bromate in the presence of potassium bromide and hydrochloric acid (Found :  $C_6H_5$ , 43.6.  $C_8H_9O_3B$  requires  $C_6H_5$ , 46.9%).

In the foregoing work, distillation of the final products was conducted in the special flasks described in the preceding paper, and analysis of those borates containing aryl groups was carried out in the manner there outlined.

