

176. *The Preparation of Simple Organic Orthoborates.*

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The synthesis of a number of organic orthoborates has been undertaken with a view to ascertain the most convenient and economical methods of preparation. The preparation of nine hitherto unknown borates is described.

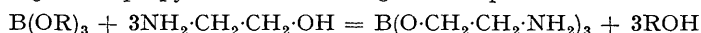
ESTERS of orthoboric acid are of some importance on account of their unique electronic structure (Yabroff, Branch, and Almquist, *J. Amer. Chem. Soc.*, 1933, **55**, 2935). In recent years patents have been taken out covering their use as plasticisers for natural and synthetic resins and cellulose derivatives, as emulsifying agents and coating compositions, and as pharmaceutical and antiseptic preparations (U.S.P.P. 1936, 2,053,474; 1941,

2,223,349; Fr.P. 1939, 848,459). It has also been stated that alkyl borates may with advantage replace alkyl chlorides in the Friedel-Crafts reaction (D.R.-P. 1930, 555,403).

The most useful methods for preparing boric esters are: (1) By refluxing a mixture of boric oxide and an alcohol with an inert solvent such as toluene, and allowing the condensed vapours to percolate through anhydrous copper sulphate held in the thimble of a Soxhlet extractor to remove the water formed during the reaction (Dupire, *Compt. rend.*, 1936, **202**, 2086). (2) By azeotropic removal of the water of reaction (Johnson and Tomkins, *Org. Synth.*, 1933, **13**, 16). (3) By alcoholysis (Schiff, *Annalen*, Suppl., 1867, **5**, 183; Wuyts and Duquesne, *Bull. Soc. chim. Belg.*, 1939, **48**, 77).

Method (1) is the most convenient for preparing quantities of 20–100 g., and it has been extended to the preparation of aryl borates. For the preparation of larger amounts, it is best, where possible, to employ method (2). In the case of alkyl borates, the water is removed continuously as a binary azeotrope with the alcohol used. This involves the use of slight excess of the alcohol. (Alternatively, a subsidiary inert liquid such as benzene, toluene, or carbon tetrachloride may largely replace the excess alcohol.) The water is then removed as a ternary azeotrope composed of water, the alcohol, and the subsidiary liquid. The method has been successfully employed by the author for the preparation of aryl borates which hitherto have been prepared by less convenient methods. In this case subsidiary liquids such as toluene and xylene possessing a b. p. higher than that of water are best used, the water being removed by distillation with the toluene or xylene.

Method (3) can be employed in the preparation of those borates which cannot be obtained by methods (1) and (2). For instance, β -aminoethyl alcohol does not react with boric anhydride under the conditions prevailing in methods (1) and (2). However, β -aminoethyl borate has been prepared simply by distilling a mixture of the ethanolamine with the borate of a more volatile alcohol, e.g., tri-*n*-propyl borate, according to the equation



The reaction was employed by Wuyts and Duquesne (*loc. cit.*), who distilled a mixture of the alcohol or phenol with a 25% excess of *n*-propyl borate. The bulk of the propyl alcohol was removed by distillation at atmospheric pressure, and the last traces together with the excess of propyl borate at reduced pressure. In the present work, a slight excess of the alcohol or phenol has been used in place of the excess of borate.

EXPERIMENTAL.

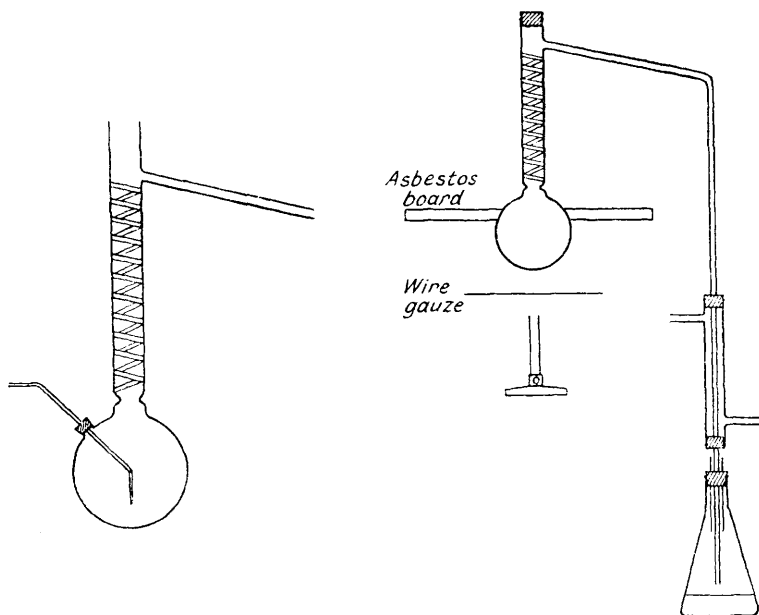
Distillation flasks of special design having advantages over the usual type were used (see Fig.). They had long necks fitted with solid glass spirals. The bulbs carried side tubes in which air leaks could be placed. Some of the borates possessed high m. p.'s, and so tended to crystallize out in the side arm during distillation. Accordingly, some of the flasks were fitted with wide side arms to prevent obstruction.

The boron content in aryl borates and in those containing basic or acidic groups could not be determined in the usual way by titration against sodium hydroxide in the presence of glycerol, owing to the acid or basic nature of the liberated phenol or alcohol. For such borates, the following method was found satisfactory. A known weight of the borate was washed into a distillation flask of the type described above with 50 c.c. of pure methyl alcohol containing two drops of pure concentrated sulphuric acid. About 20 c.c. were distilled over through a condenser into a receiving flask which contained 50 c.c. of boiled-out distilled water. After addition of glycerol or mannitol, the contents of the receiver were titrated against carbonate-free sodium hydroxide with phenolphthalein as indicator in the usual way. The process was then repeated, a second 10 c.c. being distilled off, and the contents of the flask again titrated. In this way it was found that the first distillation brought over nearly all of the boron as an azeotrope of methyl alcohol and methyl borate. The process was again repeated if necessary until no more sodium hydroxide was required to neutralise the boric acid formed in the receiver.

To determine whether or not sulphuric acid was carried over under these conditions, the process was conducted in the absence of a borate. A distillate of 50 c.c. was found to be absolutely neutral.

The analytical results for cyclohexyl borate, known to be pure from the usual method of analysis, is given as proof of the accuracy of the above method:

Weight of cyclohexyl borate taken, g., 0.3505.
 Total volume of distillate, c.c., 20, 30, 40.
 Total volume of 0.07092N-NaOH needed, c.c., 15.80, 15.95, 16.00.
 Boron found, 3.50%. Boron calculated, 3.51%.



The following borates have not hitherto been prepared.

1-Methylisoamyl (Methylisobutylcarbinyl) Borate, $B(O\cdot CHMe\cdot CH_2\cdot CHMe)_3$.—10.5 G. of boric anhydride (1 mol.), 92 g. (6 mols.) of methylisobutylcarbinol (b. p. 130—131°), and 100 c.c. of pure benzene were placed in a round-bottomed flask fitted with a Soxhlet extractor, a condenser, and thermometer placed so as to register the temperature of the vapours. 40 G. of anhydrous copper sulphate were placed in the Soxhlet. In place of the usual thimble, it was found that a plug of glass wool at the bottom of the Soxhlet sufficed to retain the copper sulphate.

After 4—5 hours of refluxing, the temperature had risen from 72° to a constant value at 80°. This indicated almost complete disappearance of the hexyl alcohol, and completion of reaction. After removal of the benzene by distillation at atmospheric pressure, the reaction mixture was fractionated under reduced pressure. This gave 84 g. (90%) of the required borate, b. p. 130—131°/17 mm. It is a clear colourless liquid. In common with all the organic orthoborates examined, it is hygroscopic and readily hydrolysed by atmospheric moisture (Found: B, 3.44. $C_{18}H_{39}O_3B$ requires B, 3.44%).

β -Methylallyl Borate, $B(O\cdot CH_2\cdot CMe\cdot CH_2)_3$.—This ester was similarly prepared from 14 g. of boron trioxide, 90 g. of β -methylallyl alcohol (b. p. 112—113°), 130 c.c. of toluene, and 40 g. of anhydrous copper sulphate. After 3 hours' heating, the temperature had risen from 83° to 110° (constant). The toluene was removed by distillation through an eight-pear column, and the residue fractionated to give 80 g. of borate, b. p. 220—226°. It solidified on cooling to a mass of colourless crystals, m. p. 28—29° (Found: B, 4.80. $C_{12}H_{21}O_3B$ requires B, 4.83%).

p-Chlorophenyl Borate.—In this case reaction was slow. 12 G. of boric anhydride (1 mol.), 128 g. (6 mols.) of p-chlorophenol, and 130 c.c. of toluene were refluxed through 50 g. of anhydrous copper sulphate for 15 hours, until the thermometer registered 100°. Fractionation under reduced pressure yielded 47 g. of unreacted p-chlorophenol and 50 g. (38%) of p-chlorophenyl borate, b. p. 258—260°/5 mm., as a highly viscous, pale green liquid which slowly solidified to a mass of crystals, m. p. 60—64° (Found: B, 2.73. $C_{18}H_{12}O_3Cl_3B$ requires B, 2.75%).

p-Methoxyphenyl Borate.—This was similarly prepared from 2.4 g. of trioxide, 25 g. of p-methoxyphenol, and 100 c.c. of benzene. The mixture was refluxed for 7 hours, and then fractionally distilled, yielding 10 g. (40%) of borate, b. p. 288°/7 mm. The product solidified on cooling to a mass of colourless crystals, m. p. 43—45° (Found: B, 2.81. $C_{21}H_{21}O_6B$ requires B, 2.84%).

Tri-o-phenylene Diborate, $C_6H_4(O\cdot B\langle O \rangle C_6H_4)_2$.—23 G. of boric anhydride, 110 g. of catechol, and 200 c.c. of toluene were refluxed through 80 g. of anhydrous copper sulphate until the thermometer registered a constant temperature of 110° (6 hours). On fractionation, 80 g. (68%) of the borate were obtained, b. p. 240—242°/7 mm. It solidified to a mass of colourless crystals, m. p. 99—104° (Found: B, 6.18. $C_{18}H_{12}O_6B_2$ requires B, 6.20%).

1-Carbo-n-propoxyethyl Borate, $B(O\cdot CHMe\cdot CO_2Pr)_3$.—This was prepared in a rather impure condition from 10 g. of boric anhydride (1 mol.), 113 g. (6 mols.) of n-propyl lactate, 150 c.c. of benzene, and 40 g. of anhydrous copper sulphate in the usual way (constant temperature of 80° after 12 hours). A fraction consisting of impure borate, b. p. 160—175°/5 mm., was obtained on distillation. It was redistilled over 2—3 g. of solid sodium hydroxide, and 20 g. of the borate were collected at 169—175°/5 mm., as a colourless viscous liquid. Boron was determined by the method described above (Found: B, 2.73. $C_{18}H_{33}O_9B$ requires B, 2.67%). Then 0.4563 g. of ester was dissolved in cold water and titrated against 0.07092N-sodium hydroxide using phenolphthalein as indicator in the presence of glycerol. Titration was then continued in the hot, the alkali being added 0.5 c.c. at a time, until a permanent red colour was obtained. This extra alkali, *i.e.*, that necessary to hydrolyse the propyl lactate, was 46 c.c. (Calc. 48 c.c.).

p-Tolyl Borate.—A mixture of 11.7 g. of boric anhydride (1 mol.), 108 g. of p-cresol (6 mols.), and 200 c.c. of toluene was slowly distilled through an eight-pear column. Successive 100-c.c. portions were taken off, the top layer being each time returned to the reaction vessel. After 5—7 distillations, the volume of water brought over reached the theoretical volume of 9 c.c., and all the boron oxide had disappeared. The reaction mixture on fractionation gave 89 g. of p-tolyl borate, b. p. 248—250°/12 mm. It slowly set to a mass of pale yellow crystals, m. p. 58—61° (yield, 80%) (Found: B, 3.28. $C_{21}H_{21}O_3B$ requires B, 3.26%).

β -Aminoethyl Borate.—94 G. of n-propyl borate were mixed with 120 g. of ethanolamine in a flask fitted with a one-foot column. Slow distillation gave 105 c.c. of distillate, b. p. 99—105°. The residue was fractionated to yield 58 g. of β -aminoethyl borate, b. p. 126—127°/8 mm. It quickly solidified to a mass of colourless crystals, m. p. 95—98° (yield, 60%) [Found: NH_2 , 25.4. $C_6H_{12}BO_3(NH_2)_3$ requires NH_2 , 25.1%]. The amino-groups were determined by titration against hydrochloric acid with methyl-red as indicator.

o-Chlorophenyl Borate.—This was prepared by a variation of method (3), for o-chlorophenol does not react with boric anhydride. 12 G. of boric anhydride, 128 g. (6 mols.) of o-chlorophenol, 73 c.c. of n-propyl alcohol, and 130 c.c. of toluene were refluxed through 50 g. of anhydrous copper sulphate for 3—4 hours until the thermometer reading was constant. The product was then distilled through a column to remove toluene and propyl alcohol, and the residue fractionated in a vacuum. 45 G. of o-chlorophenyl borate were collected at 242°/6 mm. as a viscous oil which slowly solidified to a mass of colourless crystals, m. p. 47—49° (yield, 34%) (Found: B, 2.70. $C_{18}H_{12}O_3Cl_3B$ requires B, 2.73%).

An attempt was made to prepare the borate of o-acetamidophenol by distilling slowly a mixture of 25 g. of the phenol and 40 c.c. of n-propyl borate, from an oil-bath heated to 160—190°. Some 10 c.c. of n-propyl alcohol distilled off at 96—99°, followed by a second fraction at 170—200°. The latter fraction was washed with three 100-c.c. portions of water to remove unchanged propyl borate. 18 G. of a colourless heavy oil remained; b. p. 203—205°. When a solution of this in dilute hydrochloric acid was kept for several hours, a crystalline precipitate of o-acetamidophenol, m. p. 202—204°, separated. The heavy oil was therefore identified as 2-methylphenoxazole, so alkyl borates may possibly be used with advantage as mild reagents for bringing about condensations attended by the elimination of water.

tert.-Alkyl borates cannot be prepared by the above methods.

All the borates considered above are freely soluble in benzene, toluene, ether, carbon tetrachloride, and acetone. Those borates which are liquid at room temperature are immiscible with water, but are more or less rapidly hydrolysed by it, the primary alkyl borates much more readily than secondary.

Owing to this sensitivity to moisture, sharp m. p.'s could not easily be obtained for the solid borates. The following proved to be the most satisfactory method. A few large crystals were transferred as rapidly as possible to the bottom of a dried narrow test-tube, and powdered by means of a glass rod. The tube was then drawn out to a 2-mm. diameter capillary, care being taken not to melt the sample. The capillary was broken at a convenient point, the tube sealed off, allowed to cool, and the dry crystals shaken down into the capillary. The m. p. was then determined in the usual way. Whenever possible, the m. p. so obtained was confirmed by the cooling-curve method on the bulk sample. Such a procedure was rarely practicable on account of the high degree of supercooling characteristic of most of the borates.