

THE ESTERIFICATION OF ORTHOBORIC ACID*

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In attempts to prepare tri-, di-, and monocyclohexyl borates by refluxing orthoboric acid with 3, 2, and 1 moles of cyclohexanol, the products obtained were tricyclohexyl borate, a mixture of undetermined composition and tricyclohexoxyboroxole, respectively.

Reaction between 1 and 2 moles of cyclohexanol with 3 moles of orthoboric acid led to the formation of tricyclohexoxyboroxole and metaboric acid.

With 3 moles of cyclohexanol a quantitative yield was obtained of tricyclohexoxyboroxole, which on refluxing with excess cyclohexanol formed tricyclohexyl borate. On refluxing the borate ester with boron anhydride the original tricyclohexoxyboroxole was obtained.

In refluxing toluene, metaboric acid is formed when the molar ratio of orthoboric acid to cyclohexanol exceeds 1:1, because all the cyclohexanol is converted to cyclohexoxyboroxole and the excess orthoboric acid is dehydrated to metaboric acid. In a control experiment orthoboric acid was found to be dehydrated under these conditions to metaboric acid.

These observations suggest that orthoboric acid is readily dehydrated to metaboric acid, excess orthoboric acid with cyclohexanol forms metaboric acid and tricyclohexoxyboroxole, from which tricyclohexyl borate is formed on treatment with excess alcohol, it is suggested that the esterification involves the dehydration of orthoboric acid to metaboric acid, which then forms the monomer cyclohexyl metaborate which immediately isomerizes to the trimer, tricyclohexylboroxole, a compound which on further treatment with excess alcohol gives as the final product tricyclohexyl borate.

It is essential in the reaction between boron oxide and tricyclohexyl borate that the oxide be the fluffy porous reactive type as prepared by Lange's¹ method. The dehydration of orthoboric acid by any other means forms a vitreous unreactive oxide. Likewise commercial boron oxide gives poor yields compared to the freshly prepared oxide.

Experimental

Series 1.—In (a), (b), and (c) cyclohexanol, orthoboric acid, and benzene were heated in an azeotropic apparatus (Anderson *et al.*² until the evolution of water was complete. On removal of the solvent, the residue was either distilled or recrystallized from benzene. Molecular weights were determined by hydrolysis of sample with warm water followed by titration with 0.1N barium hydroxide solution using phenolphthalein and neutral red as indicators (see Table 1). (Found for (c): C, 57.2; H, 8.7; O, 30.5; B, 3.6%. Calc. for $C_{18}H_{36}O_3B_3$: C, 57.1; H, 8.7; O, 30.6; B, 3.6%). (d) Tricyclohexoxyboroxole (c) (0.15 mole) was refluxed with excess cyclohexanol until water was no longer removed as an azeotrope. Excess cyclohexanol was removed by

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¹ Lange, W., "Inorganic Syntheses," Vol. 11, p. 22. (McGraw-Hill: New York 1946.)

² Anderson, J. R., *et al.*, *J. Appl. Chem.* 1952, **2**, 241.

distillation and the crude product recrystallized from benzene gave tricyclohexyl borate, m.p. and mixed m.p. 56.4° (Found: B, 3.6%. Calc. for $C_{18}H_{33}O_3B$: B, 3.5%). Yield 44 g (95%).

TABLE 1

Mole Ratio of Cyclohexanol to Boric Acid	Product Yield (g)	Melting Point	Molecular Weight	% B Found	% B Calculated for
(a) 0.3-0.1 mole	31 (91%)	56.4°	306	3.6	$C_{18}H_{33}O_3B$ 3.6
(b) 0.2-0.1 mole	20	$156-160^\circ$	—	9.5	$C_{12}H_{23}O_3B$ 4.8
(c) 0.1-0.1 mole	11.6 (92%)	$166-167^\circ$	383	8.6	$C_{18}H_{33}O_6B_3$ 8.6

Series 2.—(a) For reaction of 3 moles cyclohexanol with 3 moles of orthoboric acid see Series 1 (c).

(b) Cyclohexanol (0.2 mole) and orthoboric acid (0.3 mole) were refluxed with toluene until there was no further removal of water. The toluene insoluble precipitate was filtered. Yield 4 g (91%) (Found: B, 24.8%. Calc. for HO_2B : B, 24.2%). Molecular weight determined by ebullioscopic method in glacial acetic acid (Found: B, 42%. Calc. for HO_2B : B, 43.8%), unchanged on determination admixed with metaboric acid prepared in (d) below. On removal of the toluene a white crystalline product was obtained which was recrystallized from benzene, yield 22 g (90%), m.p. 167° , undepressed on admixture with authentic sample of tricyclohexoxyboroxole (Found: B, 8.6%. Calc. for $C_{18}H_{33}O_6B_3$: B, 8.6%).

(c) Cyclohexanol (0.1 mole) and orthoboric acid (0.1 mole) were refluxed with toluene to complete removal of evolved water. As in (b) metaboric acid, yield 8.5 g (97%), and tricyclohexoxyboroxole, yield 11 g (88%), were sole products of the reaction.

(d) Orthoboric acid was heated in an oven at $110^\circ C$ to constant weight. Yield 6.8 g (98.6%) (Found: B, 24.7%. Calc. for HO_2B : 24.7%. Molecular weight was determined ebullioscopically in glacial acetic acid (Found: 44.8%. Calc. for HO_2B : 43.8%).

(e) Orthoboric acid (5 g) was heated under fractionation column fitted with McIntyre weir reflux ratio heat (McIntyre³) until evolution of water was complete. The still pot residue was filtered, washed free of solvent with light petroleum (40–60° boiling range), and dried *in vacuo*. Yield 3.2 g (91%) (Found: B, 24.7%. Calc. for HO_2B : B, 24.7%).

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³ McIntyre, R. J., *Chem. & Ind.* 1933, 578.