REACTIONS OF CARBOHYDRATES, INCLUDING CELLULOSE, WITH BORON ALKOXIDES UNDER ANHYDROUS CONDITIONS

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ABSTRACT

The reactions under anhydrous conditions of methyl α-D-glucoside, methyl α-D-mannoside, sucrose, cellobiose, *O*-methylcellulose, and purified cotton cellulose with such boron alkoxides as boron ethoxide, boron propoxide, and boron isopropoxide were investigated. The neat boron alkoxide, or a solution of the alkoxide in the parent alcohol, benzene, pyridine, ethylenediamine, or pyridine–ethylenediamine was used as the solvent in different experiments. With increase in molecular weight, reaction of the carbohydrate with boron alkoxides (neat, in benzene, or in the parent alcohol) either did not occur or was decreased, its extent being very low for higher members. In pyridine or ethylenediamine, the reactivity of carbohydrates toward boron alkoxides was increased. Cellulose did not react with the neat alkoxides, and, in pyridine, reacted with them to only a small extent, but in ethylenediamine, cellulose (both ground and in fiber form) reacted with the alkoxides.

NTRODUCTI ON

The reactions and properties of carbohydrate derivatives containing boron are of particular interest in studies on modification of the rate of oxidation of carbohydrates[1,2]. When boron-containing compounds are applied to cellulosic textile materials, these materials become flame-resistant. Also, the ionization of boric acid is increased in solutions containing carbohydrates[3–5]; this effect has been used in the separation of borate complexes of carbohydrates by differential elution from columns of ion-exchange resins[6] or by paper ionophoresis[7]. Alkyl borates of carbohydrates are used in Friedel–Crafts reactions[8].

In the present work, the reactions of carbohydrates with boron alkoxides under anhydrous conditions were investigated. The compositions of the products indicated the nature of the interaction of the boron alkoxides with the various carbohydrates.

RESULTS AND DISCUSSION

The interaction of boron alkoxides with carbohydrates decreased as the molecular weight of the carbohydrate increased. Partial methylation of cellulose increased

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the reactivity of the remaining free hydroxyl groups; however, the molecular weight of the cellulose skeleton was decreased by methylation. The use of such bases as pyridine or ethylenediamine increased the extent of interaction of boron alkoxides with carbohydrates. When cellulose (mol. wt. 700,000) was used, interaction with boron alkoxides occurred only in ethylenediamine.

The products of reaction of boron alkoxides with carbohydrates are, apparently, Lewis acids, and they react with such bases as ethylenediamine[9–12]. These properties may be related to the electrophilic character of the D-glucopyranoid ring. Boron alkoxides are generally electron-deficient, and they would tend to withdraw electrons from the D-glucopyranoid ring, which is normally an electron sink[13–16]. These effects would presumably decrease the rate of oxidation of the pyranoid ring. The reaction products are readily hydrolyzed by water.

EXPERIMENTAL

Materials. — Ethanol, propyl alcohol, and isopropyl alcohol (analytical grade) were used in the preparation of the boron alkoxides. Anhydrous alcohols were prepared by azeotropic distillation with benzene (25 ml in 1 liter of alcohol), and were then stored under dry nitrogen (obtained by passing nitrogen through a train containing glass wool, silica gel, and phosphorus pentaoxide) until used. Pyridine and ethylenediamine were each kept over an excess of potassium hydroxide pellets for 24 h, then boiled for 1 h under reflux and cooled, and the upper layer was removed; this procedure was repeated. The bases were then distilled over sodium metal; fractions of the bases were collected (b.p. ~110–115°/760 torr). After adding benzene and alcohol, the anhydrous bases were prepared by azeotropic distillation. Benzene and petroleum ether (analytical grade) were dehydrated as needed. The boric acid used was of analytical grade.

Boron ethoxide was prepared by the esterification of boric acid with ethanol[17–19]. Boric acid (30 g) was dried for 1 h at 100°/0.3 torr in a round-bottomed reaction flask; then anhydrous ethanol (100 ml) and dehydrated benzene (100 ml) were added. The mixture was boiled under reflux; periodically, the lower layer of the ternary azeotrope, which contained the water produced, was removed. When the temperature reached 67°, more benzene and ethanol were added, to ensure removal of water. The binary azeotrope of benzene and ethanol was collected at 67° until the temperature increased rapidly to 80°; then more benzene was added to effect removal of the ethanol. The boron ethoxide fraction, b.p. 117–118°/760 torr, was collected.

Anal. Calc. for $C_6H_{15}B_3$: B, 7.41. Found: B, 7.37.

Boron isopropoxide was similarly prepared, by the esterification of boric acid with isopropyl alcohol[17–19]. The boron isopropoxide fraction, b.p. 138–141°/760 torr, was collected.

Anal. Calc. for $C_9H_{21}B_3$: B, 5.75. Found: B, 5.64.

Boron propoxide was prepared from boron isopropoxide by the interchange method, in which isopropyl alcohol was removed as the benzene–isopropyl alcohol azeotrope[17].

Methyl α-D-glucoside, methyl α-D-mannoside, sucrose, and cellobiose (analytical grade) were obtained from commercial, chemical-supply houses and, after drying, used without further purification. *O*-Methylcellulose having a methoxyl content of 28% (degree of substitution 1.7) was obtained from a commercial source. Deltapine cotton in the form of 7s/3 yarn was purified by the method of Arthur and Mares[20] to yield cellulose (mol. wt. 700,000).

Methods. — The reactions were conducted by placing a weighed amount of the carbohydrate in a round-bottomed flask fitted with a reflux condenser. The carbohydrate was dried by heating the flask for 1 h in an oil-bath at 70°/0.3 torr. Then, boron alkoxide and, in some cases, the corresponding alcohol or the base, or both, were added, and the mixture was boiled under reflux, the temperature of the oil-bath being maintained at 30–50° above the b.p. of the mixture. After the desired time, the alcohol produced was removed by azeotropic distillation with benzene, and then the remaining volatile compounds were removed by heating the mixture at 0.3 torr.

The boron content of the alkoxide or reaction product was determined by hydrolysis of the alkoxide or product, followed by reaction with an excess of sodium hydroxide, and heating to remove any traces of amines. Then, the excess of base was removed by filtration. The sodium–boric acid complex, in the solid state, was neutralized with 0.1 M hydrochloric acid, with Methyl Red as the indicator. The boric acid liberated, now in solution, was titrated with 1 M sodium hydroxide in the presence of glycerol, with phenolphthalein as the indicator[21]. The alkoxide content of the reaction product, in the absence of amines, was determined by the chromic acid method[22]. The concentration of ethylenediamine was determined by titration with 0.1 M hydrochloric acid, with Methyl Red as the indicator.

Methyl α-D-glucoside with boron isopropoxide. — Methyl α-D-glucoside (8 g) and boron isopropoxide (25 ml) were added to benzene (100 ml) in a 200-ml flask fitted with a small column and distillation head. The solution was then boiled under reflux, and the isopropyl alcohol liberated was removed by azeotropic distillation. When all of the alcohol had been removed, the remaining volatile compounds were distilled off at 100°/0.3 torr, and the solid product was analyzed.

Anal. Calc. for $(CH_3)(C_6H_7O_6)[B(OC_3H_7)_2]_4$: B, 6.13. Found: B, 6.12.

This product was soluble in benzene after two months of storage. When it was then heated at 100°/0.3 torr, two molecules condensed to yield boron isopropoxide and $[B(OC_3H_7)_2][B(OC_3H_7)](CH_3)(C_6H_7O_6)[B(OC_3H_7)](C_6H_7O_6)(CH_3)[B(OC_3H_7)][B(OC_3H_7)_2]$.

Anal. Calc.: B, 6.38; OC_3H_7, 48.8. Found: B, 6.43; OC_3H_7, 49.1.

Methyl α-D-mannoside with boron isopropoxide. — Methyl α-D-mannoside (5 g) and boron isopropoxide (25 ml) were added to benzene (100 ml) as already described, the solution was boiled under reflux, the alcohol formed was removed by azeotropic distillation, and the remaining volatile compounds were removed at 100°/0.3 torr. The solid product was analyzed.

Anal. Calc. for $(CH_3)(C_6H_7O_6)[B(OC_3H_7)_2]_4$: B, 6.13. Found: B, 6.09.

This product was dissolved in the minimal volume of benzene at 78°, petroleum ether was added until a small precipitate formed, the solution was cooled to 25°, and a white product (yield ~80%) was obtained. After isolation, this product was not completely soluble in benzene at 25°. The soluble fraction was recovered as solid after removal of the benzene at 25°/0.3 torr.

Anal. Calc. for $(CH_3)(C_6H_7O_6)[B(OC_3H_7)]_2$: B, 6.56. Found: B, 6.62.

Sucrose with boron propoxides. — To a solution of sucrose (3 g) in pyridine (50 ml) at 70° were added boron propoxide (25 ml) and benzene (25 ml), and the solution was then boiled under reflux. Propyl alcohol was removed by azeotropic distillation, and the remaining volatile compounds were removed at 40°/0.3 torr. The solid product was analyzed.

Anal. Calc. for $(C_{12}H_{14}O_{11})[B(OC_3H_7)_2]_8$: B, 6.33. Found: B, 6.39.

Ethylenediamine (10 ml) was added to this product at 70°, and the volatile compounds were removed at 40°/0.3 torr.

Anal. Calc. for $(C_{12}H_{14}O_{11})[B(OC_3H_7)]_8(N_2C_2H_6)_4$: B, 7.69; $N_2C_2H_6$, 20.64. Found: B, 7.65; $N_2C_2H_6$, 20.77.

Sucrose (3 g) was dissolved in pyridine (35 ml) at 70°, boron propoxide (25 ml) was added, and the solution was kept overnight at 25°, giving white solid product from which the volatile compounds were removed at 50°/0.3 torr. The product was not soluble in benzene. When boron propoxide (10 ml) was added and the solution was heated to 80°, the product dissolved. The suspension was filtered through sintered glass, and the volatile compounds were removed at 50°/0.3 torr.

Anal. Calc. for $(C_{12}H_{14}O_{11})[B(OC_3H_7)]_4$: B, 7.05. Found: B, 6.97.

Sucrose (2 g) was dissolved in pyridine (25 ml) at 70°, boron isopropoxide (20 ml) saturated with ethylenediamine was added at 70°, the solution was boiled under reflux for 10 h, and the volatile compounds were removed at 60°/0.3 torr. The product was analyzed.

Anal. Calc. for $(C_{12}H_{14}O_{11})[B(OC_3H_7)]_4(N_2C_2H_6)$: B, 6.47; $N_2C_2H_6$, 8.68. Found: B, 6.84; $N_2C_2H_6$, 8.91.

Sucrose (2 g) was dissolved in ethylenediamine (15 ml) at 70°, and boron propoxide (25 ml) was added; on cooling, a solid product formed. The clear, supernatant liquor was decanted, and the volatile compounds were removed at 70°/0.3 torr.

Anal. Calc. for $(C_{12}H_{19.5}O_{11})[B(OC_3H_7)_2]_{2.5}(N_2C_2H_6)_{2.5}$: B, 3.35; $N_2C_2H_6$, 17.97. Found: B, 3.33; $N_2C_2H_6$, 17.6.

Cellobiose with boron ethoxide. — To a solution of cellobiose (2 g) in pyridine (50 ml) at 110° was added boron ethoxide (50 ml) dropwise during 0.5 h, and, after 1 h, benzene (30 ml) was added to this clear solution. The solution was boiled under reflux, distillate (35 ml) was removed dropwise, the solution was cooled to 25°, and the supernatant liquor was decanted. The solid residue was dissolved in benzene (25 ml), boron ethoxide (10 ml) was added, and the mixture was heated for 2 h at 90°, cooled to 25°, and the supernatant liquor decanted. The remaining volatile compounds were removed at 70°/0.3 torr.

Anal. Calc. for $(C_{12}H_{14}O_{11})[B(OC_2H_5)]_3[B(OC_2H_5)_2]_2$: B, 7.69; OC_2H_5, 44.82. Found: B, 7.76; OC_2H_5, 47.35.

O-Methylcellulose with boron ethoxide and propoxides. — *O*-Methylcellulose (5 g) and boron ethoxide in ethanol (75 ml of 70% solution) were added to benzene (100 ml), and the mixture was boiled under reflux, ethanol being removed by azeotropic distillation. The remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 6.98. This proportion of boron requires trisubstitution of cellulose. Calc. for $(C_6H_9O_6)[B(OC_2H_5)_2]_3$: B, 6.76.

This result indicates that the methoxyl groups were cleaved during the reaction, and were removed as methanol from the solution. Alternatively, a cyclic complex of boron ethoxide with *O*-methylcellulose could be formed to yield a product containing the percentage of boron found.

O-Methylcellulose (5 g) and boron propoxide (50 ml) were boiled under reflux (at ~130°) for 5 h; then benzene (25 ml) was added, the propyl alcohol was removed by azeotropic distillation, and the remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 2.02. This proportion of boron agrees with that calculated for $(C_6H_{9.8}O_{4.3})(OCH_3)_{1.7}[B(OC_3H_7)_2]_{0.5}$: B, 2.02.

This product was mixed with the distillate, boron propoxide (20 ml) was added, and the mixture was boiled under reflux (at ~130°) for 8 h.

Anal. Found: B, 2.85. This proportion of boron agrees with that calculated for $(C_6H_{9.5}O_{4.3})(OCH_3)_{1.7}[B(OC_3H_7)_2]_{0.8}$: B, 2.83.

Repetition of the foregoing procedure did not increase the percentage of boron in the product.

The product was mixed with pyridine (25 ml), and, after 2 min, boron propoxide (50 ml) was added. The solution was boiled under reflux (at ~130°) for 1 h, and then distillate (25 ml) was collected dropwise. The remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 4.10. This percentage of boron indicates complete substitution. Calc. for $(C_6H_9O_{4.3})(OCH_3)_{1.7}[B(OC_3H_7)_2]_{1.3}$: B, 3.80.

O-Methylcellulose (3.4 g), boron isopropoxide (25 ml), and pyridine (25 ml) were boiled under reflux for 2 min, and then the volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 3.50. This percentage of boron agrees with that calculated for $(C_6H_{9.2}O_{4.3})(OCH_3)_{1.7}[B(OC_3H_7)_2]_{1.1}$: B, 3.45.

This product was combined with the distillate and the mixture was boiled under reflux. About one-third of the distillate was collected dropwise, and then the remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 4.02; OC_3H_7, 42.9%. These proportions indicate complete substitution. Calc. for $(C_6H_9O_{4.3})(OCH_3)_{1.7}[B(OC_3H_7)_2]_{1.3}$: B, 3.80; OC_3H_7, 41.48.

Cellulose with propoxides. — Cotton cellulose (3.5 g), ground to pass a 20-mesh screen, was added to pyridine (30 ml). After 15 min at 25°, boron propoxide (40 ml) was added, and the mixture was boiled under reflux for 20 min. Distillate (25 ml) was then removed dropwise at 130°, and the remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 0.71. This proportion of boron agrees with that calculated for $(C_6H_{9.88}O_5)[B(OC_3H_7)_2]_{0.12}$: B, 0.70.

To a portion (3 g) of this product, ethylenediamine (10 ml) was added. After 15 min at 25°, boron propoxide (50 ml) was added, the mixture was boiled under reflux, and distillate (20 ml) was removed dropwise at 130°. The remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 4.06; $C_2N_2H_6$, 11.54. These proportions agree with those calculated for $(C_6H_{8.5}O_5)[B(OC_3H_7)_2]_{1.5}(C_2N_2H_6)_{0.75}$: B, 4.08; $C_2N_2H_6$, 10.96.

Cotton cellulose (5 g) in fiber form was added to pyridine (50 ml); after 15 min at 25°, boron isopropoxide (50 ml) was added, and the mixture was boiled under reflux for 4 h. Benzene (25 ml) was then added, and boiling under reflux was continued for 3 h. The isopropyl alcohol formed was removed by azeotropic distillation, and the mixture was boiled under reflux overnight (17 h). Benzene (25 ml) was added, the isopropyl alcohol formed was removed by azeotropic distillation, and the remaining volatile compounds were removed at 100°/0.3 torr.

Anal. Found: B, 0.31. This percentage of boron agrees with that calculated for $(C_6H_{9.95}O_5)[B(OC_3H_7)_2]_{0.05}$: B, 0.32.

Cotton cellulose (5 g) in fiber form was added to ethylenediamine (50 ml), benzene (100 ml), and ethanol (15 ml), and the mixture was boiled under reflux for 5 h, the water–ethanol–benzene azeotrope being removed by distillation. Then boron propoxide (50 ml) was added, and the mixture was boiled under reflux for 23 h. A second portion (25 ml) of boron propoxide was added, and the mixture was boiled under reflux for a further 2 h, and cooled to 25°. The liquid was decanted, and the product was washed by decantation with three 50-ml portions of benzene, and then with petroleum ether (50 ml). The liquid was decanted, and the remaining volatile compounds were removed at 50°/0.3 torr.

Anal. Found: B, 3.63; $C_2N_2H_6$, 18.86. These proportions agree with those calculated for $(C_6H_{8.5}O_5)[B(C_3H_7)_2]_{1.5}(C_2N_2H_6)_{1.5}$: B, 3.68; $C_2N_2H_6$, 19.74.

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