

## Preparation and Reactions of Mesityleneboronic Acid

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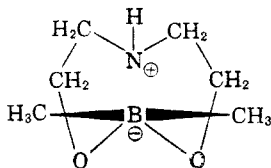
Although many aryl boronic acids and esters have been described in the chemical literature, no reference has been found to a 2,6-di-substituted phenylboronic acid. Such a material was of interest for the purpose of exploring the steric effect of 2,6 substituents upon the chemical properties of the boronic acid group. We therefore chose to prepare mesitylene boronic acid and to study its behavior in a series of common reactions.

Mesityleneboronic acid was prepared in 28% yield by the reaction of methyl borate with the mesityl Grignard reagent. The resulting boronic acid was purified by recrystallization from benzene and fully characterized. It melted sharply at 143–145° followed by resolidification and a second melting point was observed in the neighborhood of 190°. Examination of the material melting at 190° proved it to be the anhydride of mesitylene boronic acid.

Mesityleneboronic acid was smoothly converted to its *n*-butyl ester by treatment with *n*-butyl alcohol in boiling toluene. This ester was easily reconverted to mesityleneboronic acid by brief treatment with dilute sodium hydroxide solution. The lithium aluminum hydride reduction of di-*n*-butyl mesitylene boronate in ethyl ether and in the presence of pyridine at –80° afforded pyridine mesitylene borane in 78% yield. This material was normal in all respects in that it gave rapid reduction of iodine to iodide ion, silver ion to silver metal, and evolved hydrogen on treatment with dilute hydrochloric acid.

Since diethanolamine had been previously shown by Letsinger and Skoog<sup>1</sup> to afford air stable and crystalline derivatives with aryl boronic acids, several attempts were made to prepare the diethanolamine ester of mesityleneboronic acid. In each case no stable diethanolamine ester was obtained. This result is attributed to the steric inability of the diethanolamine nitrogen atom to readily coordinate with the boron atom of the diethanolamine ester to produce a tetrahedral boron atom.

Treatment of mesityleneboronic acid with hot



(1) R. L. Letsinger and I. Skoog, *J. Am. Chem. Soc.*, **77**, 2491 (1955).

dilute sulfuric acid led to the nearly instantaneous formation of mesitylene as would be expected on the basis of an electrophilic displacement reaction.

As the above results show, mesityleneboronic acid is apparently as reactive as phenyl boronic acid and similar aryl boronic acids toward anhydride formation, esterification, and reduction to the pyridine borane derivative. Only in the case of the diethanolamine ester is the steric effect of 2,6-dimethyl substitution apparent. Since there is little doubt that a steric effect does exist in reactions of mesitylene boronic acid which proceed through a transition state containing a tetrahedral boron atom, it must be concluded that such reactions of aryl boronic acids and derivatives are so rapid in general that this steric retardation goes unnoticed by the qualitative observer. This is in contrast to the observations made with mesitoic acid and its esters.

### EXPERIMENTAL

*Preparation of mesityleneboronic acid.* To a suspension of 5 g. of magnesium and a crystal of iodine in 20 ml. of ether was slowly added 40 g. (0.20 mole) of 2-bromomesitylene dissolved in 200 ml. of dry ether. This addition was carried out under nitrogen and over a 4-hr. period. The resulting mesityl-magnesium bromide was added dropwise with vigorous stirring to 21 g. of methyl borate dissolved in 200 ml. of dry ether at –78°. After the addition, the reaction mixture was allowed to warm to room temperature and to remain at that temperature overnight. The Grignard complex was decomposed by the slow addition of 200 ml. of 4*N* hydrochloric acid at 0°. The ether layer was separated, washed well with water, and dried over magnesium sulfate. Removal of the solvent under vacuum afforded an oil which was treated with two volumes of pentane. On standing the oil crystallized and 9.1 g. (28% of theory) of mesitylene boronic acid was collected by filtration. Recrystallization from benzene afforded 5.5 g. of material melting at 143–145°. Continued heating resulted in resolidification of the melt followed by the observation of a second m.p. at 193–197°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>BO<sub>2</sub>: C, 65.90; H, 7.99; B, 6.60. Found: C, 66.27; H, 8.22; B, 6.50.

*Preparation of mesitylene boronic acid anhydride.* One g. of mesityleneboronic acid was placed in a test tube and immersed in an oil bath maintained at 150°. The boronic acid rapidly melted and water vapor was seen to condense on the upper portion of the tube. Continued heating resulted in the resolidification of the melt and all residual water was removed by the application of vacuum. The resulting mesityleneboronic acid anhydride melted at 205–210° and showed no absorption in the hydroxyl region of the infrared.

*Anal.* Calcd. for C<sub>9</sub>H<sub>11</sub>BO: C, 74.04; H, 7.59. Found: C, 73.77; H, 7.61.

The anhydride was also prepared by azeotropic distillation of mesityleneboronic acid with benzene. After 8 hr. the theoretical amount of water had been collected and anhydride melting sharply at 209–210° separated from the benzene solution on cooling.

*Di-*n*-butyl mesityleneboronate.* In a Stark-Dean apparatus were heated overnight 5.5 g. of mesityleneboronic acid (0.034 mole) 50 ml. of benzene and 50 ml. of *n*-butyl alcohol. The major portion of the solvent was removed by distillation and the residual oil vacuum distilled to give 5.5 g. (59%) of ester boiling at 122–124° at 3 mm.

*Anal.* Calcd. for C<sub>17</sub>H<sub>29</sub>BO<sub>2</sub>: C, 73.92; H, 10.58. Found: C, 73.80; H, 10.21.

*Attempted preparation of the diethanolamine ester of mesityleneboronic acid.* To 100 ml. of toluene was added 4.1 g.

