

THE PREPARATION AND SOME PROPERTIES OF 2-METHYL-1-PROPENE-1-BORONIC ACID

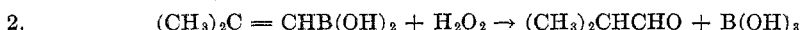
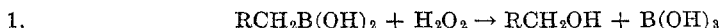
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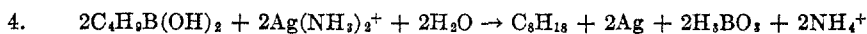
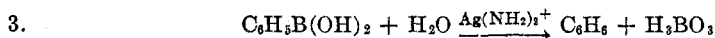
Although a considerable number of alkyl- and aryl-boronic acids have been prepared (1), only two compounds of the alkenylboronic acid type have been described. The first to be reported, β -styreneboronic acid (2), was obtained from a reaction of β -styrylmagnesium bromide with isobutyl borate, and the second, 2-chloroethyleneboronic acid (3), was formed by the catalyzed addition of boron trichloride (or boron tribromide) to acetylene, followed by hydrolysis. Work in this general field has been limited by the fact that alkenylmetallic compounds necessary for use in the classical synthetic procedure have, with the exception of the β -styryl-magnesium and -lithium compounds, been unavailable. With the recent discovery by Braude and Timmons (4), that alkenyllithium reagents can be prepared by the action of lithium on alkenyl bromides, however, this route for the preparation of the unsaturated boronic acids has been made possible. In order to obtain information concerning the feasibility of this procedure we have investigated the preparation of 2-methyl-1-propene-1-boronic acid from isobutenyllithium and methyl borate.

Isobutenyllithium was obtained in satisfactory yield (60–79%) without difficulty, and it reacted with carbon dioxide to give β -methylcrotonic acid (27% yield after recrystallization). The reaction with methyl borate, however, was less satisfactory than the analogous reactions used for the preparation of the alkaneboronic acids. Johnson and coworkers (5) isolated pure butaneboronic acid in 50% yield (60–70% yield before recrystallization) from a reaction of butylmagnesium bromide with methyl borate. We were able to duplicate their results, and furthermore, found that butyllithium could be used satisfactorily in place of the Grignard reagent. Yet the best yield of purified 2-methyl-1-propene-1-boronic acid that was realized from a reaction of isobutenyllithium with methyl borate was 7% (22% before recrystallization).

2-Methyl-1-propene-1-boronic acid, m.p. 84–86°, shows an absorption maximum at 223 $m\mu$ ($\epsilon = 1000$) in cyclohexane. As neither alkenes nor the alkaneboronic acids absorb in this region or at longer wavelengths, this property suggests a resonance interaction involving the π electrons of the carbon-carbon bond and the vacant orbital of the boron atom. Chemically, the compound exhibits properties expected for an unsaturated boronic acid. Thus, it takes up one mole-equivalent of hydrogen on catalytic hydrogenation and is oxidized readily by hydrogen peroxide. Isobutyraldehyde 2,4-dinitrophenylhydrazone was isolated from the oxidation reaction, indicating that this alkeneboronic acid undergoes oxidative cleavage similarly to the alkaneboronic acids, which are converted to alcohols by hydrogen peroxide (5) (see equations 1 and 2). With ammoniacal



silver hydroxide 2-methyl-1-propene-1-boronic acid reacts to give a 79% yield of a gaseous olefin (isobutylene) with some reduction of the silver ion to metallic silver (33% on the basis of one gram-atom of silver per mole of boronic acid). In this respect, therefore, it more nearly resembles the aromatic boronic acids, which undergo hydrolytic cleavage without reduction of silver (equation 4) than the alkaneboronic acids, which reduce ammoniacal silver ions (equation 4) (5).



EXPERIMENTAL

Isobutenyllithium. Finely divided lithium (5.8 g., 0.30 mole) was obtained by rasping the metal into a flask containing 2.2 liters of ether. Isobutenyllithium was then prepared by the addition of 40.6 g. (0.30 mole) of isobutenyl bromide dissolved in 300 cc. of ether. Our procedure differed from that described by Braude and Timmons (4) only in that finely divided lithium was employed and that a conventional mercury-sealed three-necked flask was used rather than the specially designed adapter described by Braude and Timmons. At the end of the reaction the solution was filtered through sintered glass and a portion was titrated with hydrochloric acid. The yields from several reactions as determined in this manner varied from 60–79%. In one case the isobutenyllithium solution (63% yield by titration) was forced with nitrogen pressure onto powdered Dry Ice. Isolation of acidic material yielded 9 g. (36%) of β -methylcrotonic acid, which after recrystallization from petroleum ether (b.p. 30–60°) melted at 64–66° and weighed 6.77 g. (27% yield based on the isobutenyl bromide). Braude and Timmons obtained a 14% yield of this acid by carboxylation of isobutenyllithium.

2-Methyl-1-propene-1-boronic acid. An ether solution of isobutenyllithium (0.24 mole of lithium reagent by titration) was added dropwise over a period of six hours to a solution of 40 cc. (0.26 mole) of trimethyl borate (6) in 300 cc. of ether, which was maintained at –30°. The solution was stirred vigorously and a nitrogen atmosphere was maintained throughout the reaction. After standing overnight, during which time the temperature rose to 25°, it was treated with 200 cc. of 1.5 N hydrochloric acid. The organic portion was washed several times with water, warmed to volatilize the ether, and mixed with 10 cc. of water. After this mixture had been warmed on a steam-bath and then cooled, colorless crystals of the boronic acid separated. They were dried over 65% sulfuric acid in a nitrogen-filled desiccator (weight, 5.3 g.; 22% yield based on the isobutenyllithium) and recrystallized from 75 cc. of toluene; 1.6 g. yield, m.p. 84–86°.

Anal. (by J. Sorensen) Calc'd for $\text{C}_4\text{H}_8\text{BO}_2$: C, 48.07; H, 9.08.

Found: C, 47.95; H, 8.93.

Hydrogenation. A sample of 0.3117 g. of 2-methyl-1-propene-1-boronic acid in 5 cc. of 95% ethanol was reduced by hydrogen at room temperature and atmospheric pressure in the presence of a platinum catalyst. Hydrogen was adsorbed rapidly until the consumption amounted to 104% of the theoretical amount for conversion of the methylpropeneboronic acid to isobutaneboronic acid, then the reaction ceased spontaneously. The mixture was filtered to remove catalyst, the alcohol was removed by distillation, and then 1 cc. of hot water was added. On cooling a crystalline boronic acid was deposited; wt., 0.04 g. (after drying over 65% sulfuric acid), m.p. 103–105°. Isobutaneboronic acid is reported to melt in the region of 104–112° (5).

Reaction with hydrogen peroxide. When the methylpropeneboronic acid (0.13 g.) was added to 3 cc. of 30% hydrogen peroxide, it dissolved rapidly with the evolution of heat. After the resulting solution had been warmed for five minutes on a steam-bath, it was saturated with sodium chloride and extracted with ether. A dinitrophenylhydrazine solu-

tion (7) was added to the ether extract, and the dinitrophenylhydrazone which was isolated (0.02 g.) was recrystallized several times from ethanol; m.p. 177-180°. A mixture of this material and an authentic sample of isobutyraldehyde 2,4-dinitrophenylhydrazone melted at the same temperature (177-180°).

Reaction with ammoniacal silver hydroxide. An aqueous solution (4-5 cc.) of 2-methyl-1-propene-1-boronic acid (0.095 g., 0.95 mmole, m.p. 85-86°) was mixed with an ammoniacal silver hydroxide (2.502 mmole of silver) and warmed for 30 minutes. During this time the yellow precipitate which had formed initially disappeared and black metallic silver was deposited. The free silver, which was separated, dissolved in nitric acid, and titrated with potassium thiocyanate (ferric ammonium sulfate as an indicator), amounted to 0.313 mmole, while the unreduced silver which remained in solution (determined by a thiosulfate titration in a similar manner) amounted to 2.164 mmole. On the assumption that one gram-atom of silver is reduced per mole of the boronic acid, this corresponds to reaction of 33% of the boronic acid.

The gas which was liberated during the reaction with the ammoniacal silver hydroxide was collected and analyzed for olefin content in a Blacet-Leighton apparatus (analysis by J. Rutgers). The olefin which had been formed in the reaction corresponded to 0.754 mmole of isobutylene.

SUMMARY

2-Methyl-1-propene-1-boronic acid was prepared by means of the reaction of isobutenyllithium with methyl borate. Some of the chemical and physical properties of this substance were described.

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