Studies on the Properties of Thexylboronic Acid and Its Derivatives†

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Physical and chemical properties of thexylboronic acid and its derivatives such as thexylboroxine and ethylene glycol or diethanolamine thexylboronic ester have been studied. Thexylboronic acid can be extracted from an organic solution with an aqueous sodium hydroxide solution as an "ate" complex. It is readily converted into thexylboroxine in the presence of anhydrous magnesium sulfate in pentane. It reacts with simple alcohols only slowly; however, it reacts readily with excess diethanolamine in the presence of anhydrous magnesium sulfate to give the corresponding ester.

Key Words : Property of thexylboronic acid, Thexylboroxine, Thexylboronic ester

Introduction

Thexylboron hydride, such as thexylborane[1] and thexylhaloboranes,[2] are not only useful hydroborating agents, providing important key intermediates for organic syntheses, but selective reducing agents, being extensively explored. Especially as a reducing agent, thexylboron hydrides are fascinating reagents for the aldehyde synthesis.[2e,3] Even though these thexylboron hydrides are very useful, their by-product, thexylboronic acid, is often relatively difficult to remove from the reaction mixture. The usual method is the oxidation of the reaction intermediate by alkaline hydrogen peroxide to convert it into the product and boric acid. However, this must be an undesirable procedure, particularly in cases where the reduction products are sensitive to oxidation. In these cases, the development of other simple isolation procedures is necessary. For this reason, the examination of the properties of thexylboronic acid and its derivatives is essential.

Some twenty years ago, convenient procedures for the synthesis of alkyl- and alkenylboronic acids and esters from the reactions of alkyl- and alkenyldibromo-borane-dimethyl sulfide, obtained by the hydroboration of alkene and alkynes with dibromoborane-dimethyl sulfide with water and alcohols respectively, have been published.[4] Some physical and chemical properties of boronic acids and esters have also been reported. However, studies on the hindered compounds, thexylboronic acid and esters, have been missing. Therefore, we decided to investigate the physical and chemical properties of thexylboronic acid and its derivatives in order to find out the easy way to handle it.

Results and Discussion

Preparation of Thexylboronic Acid and Its Properties. Thexylboronic acid can be easily prepared by hydrolysis of thexylborane prepared by the hyroboration of 2,3-dimethyl-2-butene with borane-dimethyl sulfide (BMS).[5] Thus, when a theoretical amount of water was added to thexylborane in diethyl ether (Et_2O) hydrogen evolved at a moderate rate and was converted quantitatively into the corresponding boronic acid. Evaporating all volatile materials gave reasonably pure thexylboronic acid (a white solid) in a quantitative yield.

Thexylboronic acid melts at just below 70 ºC (*in vacuo*). However, a true melting point seems to be meaningless because it readily loses water at around 50-55 ºC. Tetrahydrofuran (THF) dissolves it highly and Et_2O or methylene chloride can make solutions of up to 1 *M* at 25 ºC. Water dissolves it sparingly: 0.11 *M* at 25 ºC and 0.16 *M* at 100 ºC. Pure thexylboronic acid as a white solid is relatively stable in the atmosphere, showing it being only slowly oxidized. However, the acid in common solvents is sensitive to air.

Volatility on distillation was also examined in the simplified method. Thus, the slurry of 10 mmol of thexylboronic acid in 10 mL of water was distilled and the fractions of distillate was examined by ^{11}B NMR technique. Thexylboronic acid is relatively volatile. About 90% from the total amount of the acid was distilled out with 4 mL of water. Only 4% of the acid along with 5% of boric acid, the decomposed product, remained with 6 mL of water in the flask (Table 1). This would suggest that thexylboronic acid

Table 1. Volatility of Thexylboronic Acid in the Presence of Water on Distillation

Fraction mL	Content of thexylboronic acid[a] %
1	20
2	41
3	15
4	12
residue[b]	4[c]

[a]The slurry of 10 mmol of thexylboronic acid in 10 mL of water was distilled and the amount of boron compound in each fraction was determined by using an absolute value of integral of the peak on ^{11}B NMR. [b]With 6 mL of water. [c]Along with 5% of boric acid.

†This article is dedicated to the memory on the occasion of the passing (Dec. 19, 2004) of Professor Herbert C. Brown (Nobel Laureate for 1979 in Chemistry), Purdue University.

Table 2. Extraction of Thexyboronic Acid from an Organic Solution with an Aqueous Base Solution[a]

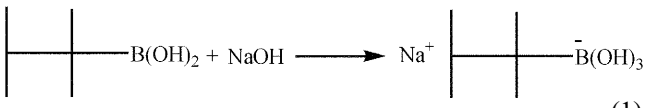
Binary system	Number of treatment	Distribution of thexylboronic acid (%)[b]	
		Organic	Aqueous
CH_2Cl_2-H_2O	first	100	0
CH_2Cl_2-1 *M* $NaHCO_3$	first	100	0
CH_2Cl_2-1 *M* Na_2CO_3	first	85	15
CH_2Cl_2-1 *M* NaOH	first	58	42
CH_2Cl_2-2 *M* NaOH	first	22	78
	second	2	98
	third	0	100
CH_2Cl_2-3 *M* NaOH	first	17	83
	second	4	96
	third	0	100
CH_2Cl_2-6 *M* NaOH[c]	first	15[d]	83
Et_2O-H_2O	first	100	0
Et_2O-1 *M* $NaHCO_3$	first	98	2
Et_2O-1 *M* Na_2CO_3	first	98	2
Et_2O-1 *M* NaOH	first	60	40
Et_2O-2 *M* NaOH	first	58[e]	42
	second	37	63
Et_2O-3 *M* NaOH	first	68[f]	32
Et_2O-6 *M* NaOH	first	71[g]	29

[a]The system of the same volume of 1 *M* solutions of thexylboronic acid in an organic solvent and base in water was stirred for 0.5 h at room temperature. [b]The content of boron compound in each phase was determined by using an absolute value of integral of the peak on ^{11}B NMR. [c]A white amorphous precipitate of the hydroxy "ate" complex formed. [d]Contained 2% of the hydroxyl "ate" complex. [e]Some hydroxyl "ate" complex was present. [f]A mixture of 56% of thexylboronic acid and 12% of the hydroxyl "ate" complex. [g]A mixture of 50% of thexylboronic acid and 21% of the hydroxy "ate" complex.

can be separated from the compounds of a lower volatility by using a simple steam distillation technique.

Extraction of Thexylboronic Acid with an Aqueous Solution of Base. Thexylboronic acid is a Lewis acid and hence it would form a complex with a base. The complex might be extractable from an organic solution into an aqueous solution. This extractability of thexylboronic acid with a base was examined and the results are summarized in Table 2.

Most part of thexylboronic acid remained, as shown in Table 2, in methylene chloride or Et_2O when treated with an aqueous solution of sodium bicarbonate or sodium carbonate. However, a sodium hydroxide in an aqueous solution formed an addition product readily with thexylboronic acid (eq. 1).



(1)

Methylene chloride appeared to be better than Et_2O because the addition product dissolves to some extent in Et_2O. Practically twice or thrice treatment of a solution of the acid in methylene chloride with a 2 *M* or 3 *M* sodium hydroxide solution resulted in a complete removal of thexylboronic acid.

Accordingly, thexylboronic acid can be effectively removed from a reaction mixture using a simple extraction only in cases where a reduction product is inert to this basic condition.

Conversion of Thexylboronic Acid into Thexylboroxine and Its Properties. The most general method for conversion of boronic acids into the corresponding boroxines is to dehydrate the acids and remove water with drying agents or on azeotropic distillation because boronic acid and boroxine exist in equilibrium.[6] Consequently, any dehydration method should shift the equilibrium in favor of the formation of boroxine. Pentane (*n*-pentane) appeared to be the best medium for this purpose. Thus, stirring the solid of thexylboronic acid with pentane for 12 min resulted in a complete disappearance of the solid and an instantaneous separation of water. The solution contained *ca*. 80% of thexylboroxine and 20% of thexylboronic acid. When anhydrous magnesium sulfate was added to the pentane layer and stirred for 5 min, it completely converted into thexylboroxine. Alternatively, stirring the slurry of thexylboronic acid in pentane in the presence of anhydrous magnesium sulfate results in a rapid conversion into its boroxine within 5 min. The pentane layer provides an essentially quantitative yield of the boroxine. However, the rate of conversion in THF or Et_2O solvent in the presence of anhydrous magnesium sulfate was very sluggish.

Thexylboroxine is very sensitive to air. It is readily hydrolyzed with water to the corresponding boronic acid. Thus, the reaction of thexylboroxine in THF or Et_2O with 3 equiv of water gives 3 equiv of thexylboronic acid immediately.

Reaction of Thexylboronic Acid and Thexylboroxine with Alcohols. The simple procedure for the preparation of simple boronic esters from the corresponding boronic acids with alcohol has been published.[4] Unhindered alkyl- and alkenylboronic esters can be prepared easily and quantitatively from the reaction with alcohols in pentane with a concurrents separation of water. We applied the same procedure to thexylboronic acid and thexylboroxine, a hindered derivative.

The reaction of the acid and boroxine with excess methanol in pentane was very slow even in the presence of anhydrous magnesium sulfate, apparently due to the steric hindrance of the thexyl group. Reaction of the acid and boroxine with ethylene glycol was also very slow; however, because of its relative stability to hydrolysis, the reaction slowly underwent the formation of ester with the separation of water. Again, the reaction of thexylboronic acid with polyols such as glycerol and sorbitol was not satisfactory. Originally we hoped that it could remove thexylboronic acid from a solution by forming a complex with polyols because such complexes are insoluble in common solvents (THF, CH_2Cl_2 and Et_2O). However, the complex formation was very slow. Furthermore, the powder of sorbitol became a lump and the ^{11}B NMR spectra of the solution looks like a boroxine, indicating thexylboronic acid loses water in the

Table 3. Formation of Diethanolamine Thexylboronic Ester From the Reaction of Thexylboronic Acid and Diethanolamine in the Presence of Anhydrous Magnesium Sulfate[a] at Room Temperature in Various Solvents[b]

Expt	Concentration of acid in solution, *M*	Equivalent of diethanolamine	solvent	Reaction time h	Yield of ester %[c]
1	1	1	THF	0.16	56
				3	57
				24	61
2	0.5	1	THF	0.16	50
				24	55
3	0.5	2	THF	0.16	66
				6	68
4	1	1	Et_2O	0.16	55
				0.5	61
5	0.5	1	Et_2O	0.16	53
				3	67
				24	71
6	0.5	2	Et_2O	0.16	70
				1	81
				3	87
				24	100
7	0.5	1	CH_2Cl_2	0.16	72
				3	80
				24	82
8	0.5	2	CH_2Cl_2	0.16	85
				0.5	90
				1	100
9	0.5	1 + 0.5[d]	CH_2Cl_2	0.16 +0.16[d]	100

[a]Equivalent of anhydrous magnesium sulfate was used. [b]The reaction mixture was stirred vigorously and a white precipitate of the ester formed immediately. [c]The yield of ester was estimated by measuring the content of thexylboronic acid remaining in solution by using an absolute value of integral of the peak on ^{11}B NMR. [d]Reacted with 1 equiv of amine for 10 min, then added an additional 0.5 equiv of amine and stirred for 10 min more.

presence of sorbitol.

Conversion of Thexylboronic Acid into the Corresponding Diethanolamine Ester and Its Properties. Several reports for the structures of cyclic boronic esters from the esterification of monoalkylboron compounds with diethanolamine have been published.[7] These esters are stabilized by an intramolecular nitrogen-boron coordination. Practically the optically active boronic acid was isolated as its crystalline diethanolamine ester from the reaction of boronic acid and diethanolamine in Et_2O.[8] In fact, such procedure works equally well to this system: diethanolamine thexylboronic ester is readily prepared. However, the rate of reaction is quite dependent upon the reaction conditions, as summarized in Table 3.

Reaction with 1 equiv of diethanolamine was not satisfactory: apparently the initially formed solid product seems to inhibit further reaction. Therefore, using excess diethanolamine is required for the complete formation. Methylene chloride appeared to be a better solvent than THF or Et_2O. Stirring the mixture of thexylboronic acid and 2 equiv of diethanolamine in the presence of anhydrous magnesium sulfate in methylene chloride provides a complete formation of the ester within 1 h at room temperature. More practically, stirring the mixture of acid and 1 equiv of diethanolamine in the presence of anhydrous magnesium sulfate for 10 min, followed by addition of an additional 0.5 equiv of amine and stirring for 10 min more results in the complete conversion of thexylboronic acid into its diethanolamine ester. Filtration and crystallization by addition of Et_2O (or pentane) give almost quantitative yield of the ester.

Diethanolamine thexylboronic ester, a white voluminous solid (mp 158-159 °C) is stable to air, but readily hydrolyzed and methanolyzed (in equilibrium with the methyl ester). It is almost insoluble in pentane and only slightly soluble in Et_2O.

Conclusion

Thexylboronic acid and its derivatives, such as thexylboroxine and ethylene glycol or diethanolamine thexylboronic ester, have been fully characterized. Thexylboronic acid can be extracted with aqueous sodium hydroxide solution from a solution of methylene chloride as an addition complex. It is readily converted into thexylboroxine in the presence of anhydrous magnesium sulfate in pentane. The reactions of the acid and boroxine with simple alcohols and polyols are slow; however, it readily reacts with excess diethanolamine in the presence of anhydrous magnesium sulfate to give the corresponding diethanolamine ester in an almost quantitative yield.

This full understanding on physical and chemical properties of thexylboronic acid and its derivatives should provide an easy and efficient way to treat a reaction mixture in which the boronic acid is involved and hence would provide a simple method for isolation of the products.

Experimental Section

All glassware used was dried thoroughly in a drying oven, assembled hot, and cooled under a stream of dry nitrogen. All reactions and manipulations of air- and moisture-sensitive materials were carried out under a dry nitrogen atmosphere. Further special experimental techniques are described elsewhere.[9]

Materials. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl just prior to use. All other liquid chemicals (methanol, methylene chloride, diethyl ether and olefin) were thoroughly dried over molecular sieves and used without further purification. Borane-dimethyl sulfide (BMS) and 2,3-dimethyl-2-butene were used directly as received from Aldrich.

Spectra. Infrared spectra were obtained with a Perkin-Elmer 1420 Ratio Recording spectrophotometer using sealed liquid cells and the two-syringe technique. ^1H NMR spectra were recorded on a Varian T-60 instrument. ^{11}B NMR spectra were recorded on a Varian FT-80A spectrophotometer. ^{11}B NMR chemical shifts are with reference to

$BF_3{\cdot}OEt_2$ (0) and assigned as positive with the resonances downfield from $BF_3{\cdot}OEt_2$.

Procedure for Determining the Content of Boron Compounds Using ^{11}B NMR. The content of each boron compound in a reaction mixture was determined by using an absolute value of integral of the peak on ^{11}B NMR. At the appropriate time period, an aliquot of reaction mixture was removed and transferred to an NMR tube. The sample was scanned, accumulated, and finally integrated by a computerized ^{11}B NMR spectrophotometer using the same parameters for the number of transients (NT), acquisition time (AT), and integral scale (IS) throughout the experiment. The value of the total integral of the peak was compared to the value of an authentic sample of which concentration was known and hence the content of boron compound of a reaction mixture was estimated. Test experiments were carried out by using several samples of different concentrations. In these cases the contents of boron compounds were in good agreement with the relative values of integral of the peaks.

Preparation of Thexylboronic Acid. In a dry, 500-mL flask fitted with a sidearm, a rubber syringe cap and a magnetic stirring bar, 30 mL of BMS (neat, 300 mmol) was placed and the flask was cooled to -10 °C in an ice-salt bath. 2,3-Dimethyl-2-butene (36 mL, 300 mmol) was then added dropwise while stirring the contents in the flask. After the addition was complete, the ice-salt bath was replaced by an ice-water bath and the reaction mixture was stirred for 2 h at this temperature. After this, the bath was removed and 50 mL of Et_2O was added to the hydroboration product. Thexylborane-dimethyl sulfide was hydrolyzed by the addition of 10.8 mL of deoxygenated water. Hydrogen evolved at a moderate rate. After the hydrogen evolution was complete, pumping off all volatile products at room temperature under aspirator vacuum gave almost pure thexylboronic acid, a white solid, in quantitative yield. The product was further purified by dissolving in Et_2O, evaporating and washing quickly with pentane. ^{11}B NMR: δ 33 ppm (THF), 34.6 ppm (Et_2O). ^{1}H NMR [$CDCl_3$ + DMSO-d_6 (1 : 1) or DMSO-d_6]: δ 0.7-1.0 ppm (1H,-CH_3, s, d), 1.5-2.0 (1H,  septet), 6.7 (2H,-O-H, broad). IR (Et_2O): 3220 cm^{-1} (-O-H, broad and strong), 1350 (B-O, strong).

The Volatility of Thexylboronic Acid in the Presence of Water. The volatility upon distillation in the presence of water was determined in the simplified method. With the usual distillation setup, connected to a mercury bubbler, a simple distillation was carried out. In a 50-mL flask, 10 mmol of thexylboronic acid and 10 mL of the deoxygenated water was placed and the flask was gently heated at such a rate that the distillate comes out dropwise. Each 1 mL of distillate was collected and the contents of the boron compound was determined by using an absolute value of integral of the peak on ^{11} B NMR.

Extraction of Thexylboronic Acid with an Aqueous Base Solution. Extraction of thexylboronic acid in methylene chloride with a 2 *M* solution of aqueous sodium hydroxide is representative. In a 100-mL flask typically equipped as above, 10 mL of a 1 *M* solution of thexylboronic acid in methylene chloride and 10 mL of a 2 *M* solution of aqueous sodium hydroxide were introduced. The contents in the flask was stirred vigorously for 0.5 h at room temperature. An aliquot of the organic layer was then transferred to an NMR tube and the sample was scanned and integrated by an ^{11}B NMR spectrophotometer with the present parameter for NT, AT and IS. The value of integral of the peak was compared to the value for a blank experiment in which 10 mL of water had been substituted for the 10 mL of sodium hydroxide solution. The difference in the value of integral represents the amount of thexylboronic acid extracted into the aqueous layer. Thus, 22% of thexylboronic acid remained in the organic layer. The ^{11}B NMR spectrum for the aqueous layer corresponded with the formation of the hydroxy "ate" complex centered at δ 2.12 ppm. After examination by ^{11}B NMR, the sample in an NMR tube was transferred to the original reaction mixture. The organic layer was separated and subjected again to the second treatment with the same volume of 2 *M* sodium hydroxide solution. The following procedures are exactly the same as above. Thus, 2% of the acid remained in the organic layer after the second treatment and a complete removal of the acid from the organic layer after the third treatment were apparent.

Conversion of Thexylboronic Acid into Thexylboroxine in the Presence of Anhydrous Magnesium Sulfate in Pentane. In a 100-mL flask fitted with the usual setup, 1.298 g of thexylboronic acid (10 mmol) and 1.2 g of anhydrous magnesium sulfate (10 mmol) were placed and 10 mL of pentane was introduced. The slurry in pentane was stirred vigorously for 5 min at room temperature and filtered. IR spectrum of the clear solution exhibited only the presence of thexylboroxine without any absorption around 3220 cm^{-1} for the O-H stretching.

A similar procedure was applied to a larger-scale reaction. In the usual assembly 38.94 g (300 mmol) of thexylboronic acid and 100 mL of pentane were placed. The slurry in pentane was stirred at room temperature. The solid disappeared in 12 min and *ca*. 3.5 mL of water separated. The turbid pentane solution was dried with a sufficient amount of anhydrous magnesium sulfate and the resulting clear solution was subjected to distillation to yield 29.85 g (89%) of pure thexylboroxine, bp 121 °C/0.3 mm, n^{20}D 1.4312. ^{11}B NMR (neat): δ 33 ppm. ^{1}H ($CDCl_3$): δ 0.7-1.0 ppm (12H, -CH_3, s, d), 1.7 (1H,  , septet). IR (neat): 2950 cm^{-1} (B-H, strong), 1290 (B-O, strong). Anal. Calcd. for $C_{18}H_{39}B_3O_3$: C, 64.38; H, 11.69. Found: C, 64.50; H, 11.98.

Esterification of Thexylboronic Acid and Thexylboroxine with Ethylene Glycol. The esterification was carried out according to the procedure developed by Brown *et al*.[5] with a slight modification. In the usual way 7.79 g of thexylboronic acid (60 mmol) was stirred with 40 mL of pentane and 3.72 g of ethylene glycol (60 mmol) for 3 h at room temperature. The solid disappeared immediately and the solution became turbid, but slowly cleared with the separation of water. The solution was dried with anhydrous

magnesium sulfate and subjected to distillation to give a 78% yield of the ester.

Exactly the same procedure was adopted for the reaction of thexylboroxine with ethylene glycol. Thexylboroxine (6.72 g, 20 mmol) was stirred with pentane (30 mL) and ethylene glycol (3.72 g, 60 mmol) for 24 h. The separated water was removed, the pentane layer was dried, and distillation gave pure ethylene glycol thexylboronic ester (7.86 g, 84%), bp 69.5-70 °C/19 mm, $n^{20}D$ 1.4278. ^{11}B NMR (neat): 35.37 ppm. ^1H NMR ($CDCl_3$): δ 0.7-1.0 ppm (12H, -CH_3, s, d), 1.5 (1H,  septet), 4.1 (4H, -CH_2-, s).

Reaction of Thexylboronic Acid with Diethanolamine in the Presence of Anhydrous Magnesium Sulfate. The general method used was to stir the mixture of thexylboronic acid and diethanolamine in the presence of an equivalent amount of anhydrous magnesium sulfate in solvent and determine the content of the acid in solution by using ^{11}B NMR technique. Reaction of thexylboronic acid with 1.5 equiv of diethanolamine with a stepwise addition in methylene chloride is typical. In a 100-mL flask with the usual setup 10 mL of 1 *M* methylene chloride solution of thexylboronic acid, 1.2 g of anhydrous magnesium sulfate (10 mmol) and 1.05 g of diethanolamine (10 mmol) were placed. The contents in the flask were stirred vigorously. A white precipitate formed immediately. After stirring for 10 min, an aliquot of the solution was subjected to determination of content of the acid by ^{11}B NMR technique, resulting in 2.8 mmol of thexylboronic acid remaining as unreacted in the solution (72% conversion). Again, 0.53 g of diethanolamine (5 mmol) was added and the contents were stirred for 10 min more. ^{11}B NMR spectrum showed the complete disappearance of thexylboronic acid and the formation of diethanolamine ester.

The same procedure was applied to a large-scale reaction. Thexylborane (100 mmol) was prepared from BMS under neat conditions as before. Hydrolyzing thexylborane with a theoretical amount of water (3.0 mL) in methylene chloride gave a thexylboronic acid solution in quantitative yield. Reaction with 1 equiv of diethanolamine in the presence of anhydrous magnesium sulfate for 10 min, followed by addition of an additional 0.5 equiv of diethanolamine and stirring for 10 min resulted in the complete conversion of the ester. After pumping off all volatile products under aspirator vacuum, a limited amount of THF was added just to dissolve the ester. Magnesium sulfate was filtered out and a sufficient amount of Et_2O (or pentane) was added to precipitate out the product (19.48 g, 98%) in almost pure form. Recrystallization from THF/Et_2O gave pure diethanolamine thexylboronic ester (92%), mp 158-159 °C, bp 188-189 °C (20 mm). ^{11}B NMR ($CHCl_3$): δ 14.97 ppm. ^1H NMR ($CDCl_3$): δ 0.7-0.95 ppm (18H, -CH_3, s, d), 1.7 (1H,  septet), 3 (4H, -CH_2-N-, m), 3.9 (4H, -O-CH_2-, t), 4.5 (1H, -N-H, broad). Anal. Calcd. for $C_{10}H_{22}O_2BN$: C, 60.32; H, 11.14; N, 7.04. Found: C, 60.24; H, 11.14; N, 7.01.

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