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Dioxaborolanes and Borates Derived from 2,3-Butanediol, Mandelic Acid, and Quinic Acid [1]

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Quinic acid **1** has pronounced biological activities in the biochemistry of plants [2], and it is also a very useful chiral raw material for total syntheses of complex molecules and chiral reagents for asymmetric syntheses [3a,b]. Its relevance is based on its four chiral centers and the five functional groups. We are currently interested in preparing boron [3c] and metallic [4] derivatives of quinic acid in order to study their structures, reactivity, spectroscopy, and their role in plant biology, especially as an uncoupler on thylakoids of spinach chloroplasts [5]. Recently, boron hydrides in five-membered rings have gained significant importance as chiral reducing agents used directly, or as catalysts, or accompanied by catalysts [6]. Investigation of the reactions of α-hydroxyacids with borane is also relevant, because the 1,4,5-dioxaborolan-2-one compounds bearing a hydride-on-boron atom are not known in the literature with the exception of the boron derivative of quinic acid [3c]. The reason for the lack of examples of these kinds of hydrides in the literature is the occurrence of a competitive reduction of the carboxyl group that takes place during the formation of the heterocycles. Herein, we report the investigation of reaction conditions under which such heterocycles can be formed without reduction.

The hydroxyacid function produces a heterocycle with a very acidic boron atom that favors strong coordination with the basic solvent as well as formation of spiro compounds.

The compounds reported here are also chiral boron hydrides, candidates to augment the growing list of new asymmetric reducing reagents. Interpretation of the structures of the reaction products is not easy due to the polyfunctionality of the quinic acid molecule, along with the insolubility, high reactivity, and moisture sensitivity of the boron compounds formed and also to the existence of equilibria. The compounds must be studied in a freshly prepared condition and with reagent ratios carefully measured. The boron hydride compounds could not be isolated owing to their high reactivity, but their formation was confirmed from the structures of the borate derivatives obtained by hydrolysis by exposure to traces of moisture. In order to understand the reactivity of quinic acid with boron reagents and to correctly assign the structures of the different compounds, we were prompted to investigate simpler molecules. Hence, we were interested in examining the reactivity of the same boron reagents with mandelic acid **2** and with 2,3-butanediol **3** (Figure 1).

These ligands helped us to model the isolated reaction sites of quinic acid at C-1 or at C-3 and C-4. The reactions investigated afforded B-H dioxaborolanes, spiroborates, and borates. The products were studied by ^{11}B NMR spectroscopy which is very sensitive to boron coordination, substituents, ring nature, steric effects, equilibrium, and solvents, and also by ^{13}C NMR spectroscopy which can help us to assign the boron connections since the carbon connected to the boron atom is normally shifted by around 6 ppm to higher frequency. The same effect has been found in dioxolane formations [3,7]. ^{1}H NMR spectroscopy is not helpful because the spectra are very complex.

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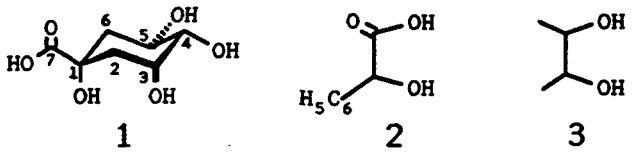

1 2 3

FIGURE 1

REACTIONS OF MODEL COMPOUNDS, 2,3-BUTANEDIOL AND MANDELIC ACID, WITH BORON REAGENTS

Reactions of Mandelic Acid 2

Compound **2** reacts with one equivalent of BH_3-THF in CH_2Cl_2 at −55°C to give the dioxaborolane **4** with a hydride function (δ = +10, d, J = 123 Hz). When the solution reached room temperature, the ^{11}B NMR spectrum showed, besides **4**, a bicyclic compound **5** (δ = +13, 5%) and compound **6** (δ = +28, d, 176 Hz, 10%).

When the reaction was performed with **2** and three equivalents of BH_3-THF, the hydride dioxaborolane **6** was formed in high yield, the carbonyl function being cleanly reduced. The reaction with 0.5 equivalents of BH_3-THF added directly to solid **2** gave principally the boraspiranic compound **8a** (δ = +12). The acidic protons react very fast with the borane, thus preventing the reduction step. The reaction of **2** with 1.5 equivalents of BH_3-THF at room temperature afforded principally compound **5**, the ^{13}C NMR spectrum showing the disappearance of the carbonyl group signal and the appearance of a methylene group signal at δ 74.0 (Figure 2).

We have also tried to synthesize the dioxaborolane **4** by the reaction of an equimolar ratio of **2** and BH_3-DMS in THF, the reaction being followed by ^{11}B NMR spectroscopy at low temperature. No reaction was observed until a temperature of −30°C was attained. At this temperature, a broad signal of **4** together with a small doublet (5%) of compound **6** was recorded. The same ratio of compounds produced was observed at 27°C. Reaction of compound **2** with 0.5 equivalent of BH_3-DMS at 60°C afforded exclusively the spiro derivative **8a**. Compound **2** was also made to react with one equivalent of BH_3-NEt_3, a less powerful borane, and the reaction was followed by ^{11}B NMR spectroscopy. When the mixture was heated to 80°C in DMSO during 12 hours, the spiranic compound **8b** was formed. It is interesting to note that the ligand was not reduced and that the amine stabilizes the anionic borate formed. Compound **8a** is a strong acid which forms a stable salt with triethylamine. Borate **8** can also be synthesized by reaction with 0.5 equivalent of $LiBH_4$ in THF **8c** or from KOH and $B(OH)_3$ in aqueous medium **8d**. In the latter reaction, the borate **9** (δ = +7) is also observed but in very low concentration (5–10%). With equimolar quantities of KOH, $B(OH)_3$, and **2**, **9** is the only compound formed. In the presence of 2 equivalents of KOH, the reaction of **2** with $B(OH)_3$ was inhibited; $KB(OH)_4$ (δ +2) and the potassium salt of mandelic acid were obtained. The spiro compounds **8d**, prepared from (S) mandelic acid, existed as two diastereoisomers (43/57), owing to the chirality of the spiranic structure. They were effectively observed by ^{13}C NMR spectroscopy. The existence of equilibria in the boron heterocyclic compounds was demonstrated by the reaction of the spiro compound **8a** with one equivalent of BH_3-DMS to give the heterocycle **4** and some borate. Reaction of compound **2** with phenylboronic acid afforded quantitatively the phenyldioxaborolane **10** identified by its ^{11}B NMR spectra (δ = +10 in DMSO or δ = +35 in $CDCl_3$). We had planned to prepare compound **12**, which could be an interesting reducing agent, by adding one equivalent of LiH to **10** in THF. The reaction produced a mixture of **10** that gives very broad signals in ^{13}C NMR, probably due to the presence of lithium, and the reduced molecule **11** (δ = +31.2 in DMSO-d_6). We did not find any evidence of the compound of structure **12**. The strong coordination of each of the dioxaborolanes **4** and **10** to basic solvents, detected by the shift to low frequency of the boron resonances, contrasts with the behavior of the dioxaborolanes **6** and **11** in which a less acidic boron atom is found. The strong acidity in compound **4** was also evidenced by the value of the coupling constant J(B–H) = 123 Hz that indicates some tetrahedral character of the boron atom, in contrast to the larger value for compound **6** J(B–H) = 176 Hz, indicative of the presence of a trigonal planar boron atom.

Reactions of 2,3-Butanediol **3**

Commercial *threo*-(2R, 3R)-(−)-butanediol **3** is contaminated by a small quantity of the *erythro*-isomer (6%). The reaction of this mixture with 3 equivalents of BH_3-THF afforded the dioxaborolane *trans* **13** (δ +28, d) (Figure 3).

From the ^{13}C NMR spectrum of the reaction products, the data of the minor isomer *cis* **13** was obtained (Table 2). When the reaction was performed with equimolar quantities of reagents, the *bis*-borolane ester **14** (δ +23) was formed. Its ^{13}C NMR data were assigned from data of **3** and **13**. The spiranic borate **15** (δ +9) was obtained by reaction of two equivalents of **3** with one of $LiBH_4$ in THF solution or in water containing $B(OH)_3$ and KOH. Spiro compound **15** has an S_2 symmetry axis, and no isomers are expected. In the latter reaction, the dioxaborolane **16** (δ +5) is also observed.

An equimolar mixture of **2**, **3**, and $LiBH_4$ gave a single signal at δ +11 which lies between the shifts for compounds **8** (+12) and **15** (+9), indicating a fast equilibrium between **8**, **15**, and **17**. The reaction of compound **3** with phenylboronic acid gave

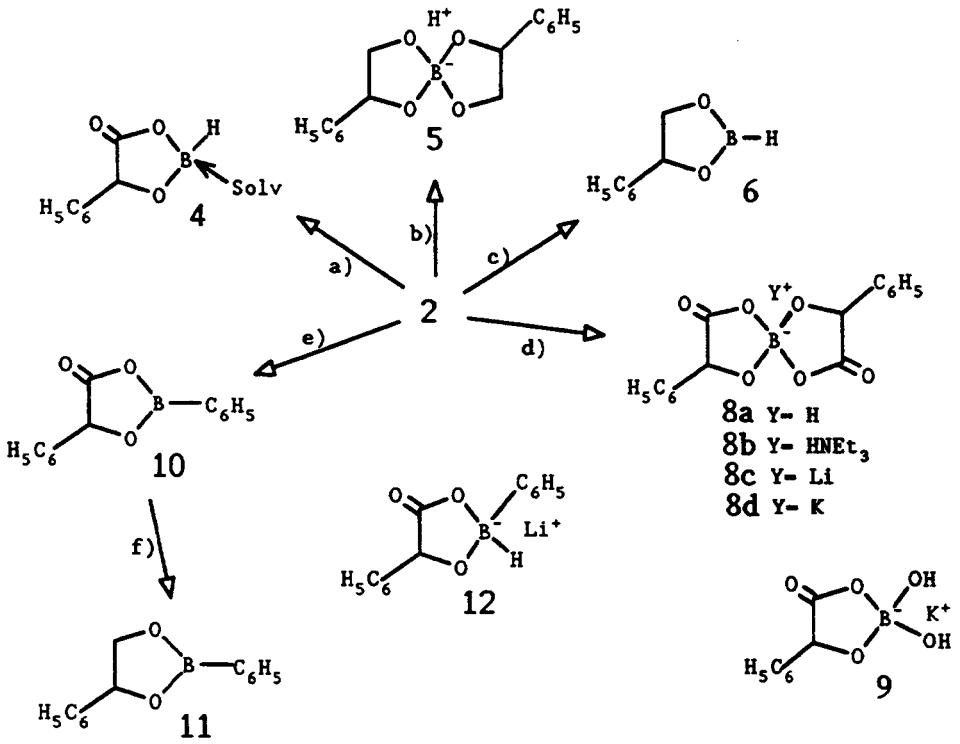

FIGURE 2 (**a**) 1 equiv BH_3-THF at −55°C or 1 equiv BH_3-DMS/THF of −30–27°C; (**b**) 1.5 equiv BH_3-THF at 27°C; (**c**) 3 equiv BH_3-THF at 27°C; (**d**) 0.5 equiv BH_3-THF or 0.5 equiv BH_3-DMS at 40°C or 1 equiv BH_3-NEt_3 at 60°C or 0.5 equiv $LiBH_4$/THF or 1 equiv KOH + 1 equiv $B(OH)_3/H_2O$; (**e**), 1 equiv $H_5C_6B(OH)_2$; (**f**) 1 equiv LiH.

TABLE 1 ^{13}C and ^{11}B NMR [δ, (J, Hz)] and IR (cm^{-1}) of Derivatives of Mandelic Acid

	^{13}C NMR							*IR*	
Compounds	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*^{11}B NMR*	*C=0*	*B–H*
2[a,b]	173.1	71.6	138.7	126.9	125.4	126.5		1714	
4[c,d]	176.5	78.2	138.3	128.0	128.0	125.6	+10 d (123)		
5[b,d]	74.0	77.4	137.0	128.2	126.2	126.5	+13 s[e]		
6[a,c]	72.8	78.6	141.2	128.9	128.8	128.3	+28 d (176)		2345
8a[a,f]	177.3	77.9	141.0	128.4	127.7	126.7	+12 s[e]		
	177.2	77.7	140.0					1805	
8b[a,f,g]	176.9	77.5	140.7	127.9	126.2	127.3	+12 s[e]		
	177.1	77.3	141.0						
8c[a,f]	177.9	77.4	140.6	128.4	126.3	128.1	+12 s[e]		
		76.8							
8d[a,f,h]	178.9	77.7	137.6				+12 s[d,e]		
	179.2	77.6	137.6						
9[a,i]	179.8	78.2	137.5	128.8	127.0	126.7	+7 s[d,e,i]		
10[a,f,j]	176.6	76.4	137.5	127.1	126.2	127.0[k]	+10 s[e,l]	1799	
11[a,f,m]	73.4	80.2	148.0				+31		

[a]67.94 MHz; [b]THF-d_8; [c]$CDCl_3$; [d]22.52 MHz; [e]broad signal; [f]DMSO-d_6; [g]ammonium carbons: 46.00, 9.65 ppm; [h]128.45, 128.39, 128.22, 126.47, 126.07; [i]D_2O; [j]B-phenyl group 131.36, 127.97, 127.37, or 127.02; [k]or 127.37; [l]+35.0 ppm in $CDCl_3$; [m]aromatic carbons: 126.89, 126.77, 127.34, 127.89, 131.86, 134.31.

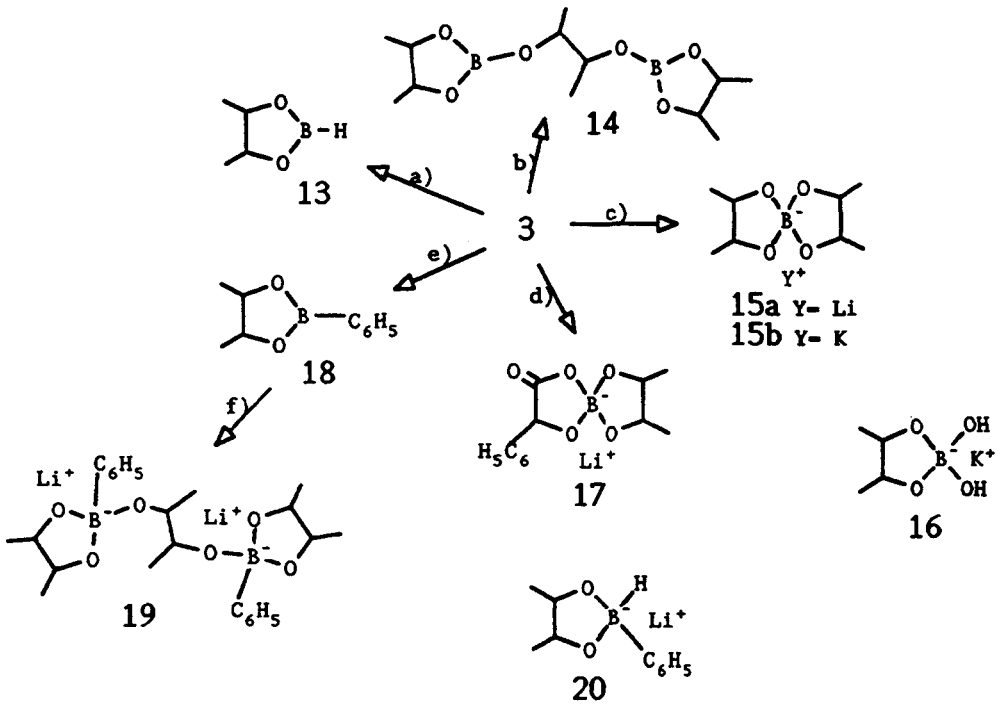

FIGURE 3 (a) 3 equiv BH_3-THF; (b) 1 equiv BH_3-THF; (c) 1 equiv $LiBH_4$/THF or 1 equiv KOH + 1 equiv $B(OH)_3/H_2O$; (d) 1 equiv **2** + 1 equiv $LiBH_4$/THF; (e) 1 equiv $H_5C_6B(OH)_2$; and (f) 1 equiv LiH.

TABLE 2 ^{13}C and ^{11}B NMR Data [δ, (J, Hz)] and IR (cm^{-1}) of 2,3-Butanediol Derivatives

	^{13}C NMR		
Compounds	*C-1*	*C-2*	*^{11}B NMR*
3cis[a,b]	70.8	16.3	
3trans[a,c]	71.1	18.0	
13trans[a,b,d]	80.1	21.1	+28 d(177)
13trans[e,c]	80.1	20.8	+27 d(177)
13cis[a,b]	75.4	16.6	+28 d(177)
14[e,f,g]			+23 s[h]
15a[a,f]	75.5	19.7	+9 s[h]
15b[e,i]	77.1	19.2	+9 s[h]
	72.7	20.3	
16[e,i]	72.7	18.4	+5 s[h]
17[d,e,f,j]	76.4	20.6	+11 s[h]
	75.5	20.2	
18cis[a,f,k]	75.5	16.5	+31 s[h]
18trans[a,f,k]	80.2	20.7	+31 s[h]
19[l]			+8 s[h]

[a]67.92 MHz; [b]$CDCl_3$; [c]THF-d_8; [d]B–H and C=O bonds of compounds **13** and **17** appear in IR at 2350 and 1807 cm^{-1}, respectively; [e]22.52 MHz; [f]DMSO-d_6; [g]signals of butanediol central group appears at 75.1 and 18.9 ppm; [h]broad signals; [i]D_2O; [j]mandelic acid: C-1 177.5, C-2 76.9, C-3 141.9, C-4 128.7, C-5 126.9, C-6 128.2; [k]aromatic: 134.67, 131.48, 127.91; [l]^{13}C spectrum is a complex mixture of isomers which were not assigned.

quantitatively the phenyldioxaborolane **18** of the *cis* and *trans* diol (δ +31) (Table 2). Addition of LiH to **18** gave a mixture of **18** and a disproportionation product, *bis*-borolane **19** (δ +8). We have not found any evidence of borohydride **20**, in spite of the fact that analogous structures have been reported [8].

From the chemical shift values of **5**, **8**, **9**, **15**, and **17**, it was deduced that the ligands have an additive effect on the ^{11}B δ of the borate function [9]. The $KB(OH)_4$ is found at δ +2.0, while the five-membered ring **16** formed with the diol is found at δ +5 in DMSO (+5.4 in H_2O) and with the α-hydroxyacid **9** at δ +7 in DMSO (+8 in H_2O). The spiranic compound **15** from the diols was found at δ +10 in DMSO (+9 in H_2O) and from the hydroxyacid **8** at +12.0 in DMSO (+10 in H_2O).

Reaction of Quinic Acid Derivatives with Boron Reagents

Owing to the structure of quinic acid **1**, different conformations and several possibilities of reaction sites can be envisaged [7]; they are shown in Figure 4: the reaction(s) with the hydroxy group on C-1 and the carboxylic function, (b) between a carboxylic group and the hydroxy group on C-5, (c) with hydroxy groups at C-1 and C-3, (d) at C-3 and C-4 or (e) at C-4 and C-5. Herein, we report the different boron hydrides and borates that were ob-

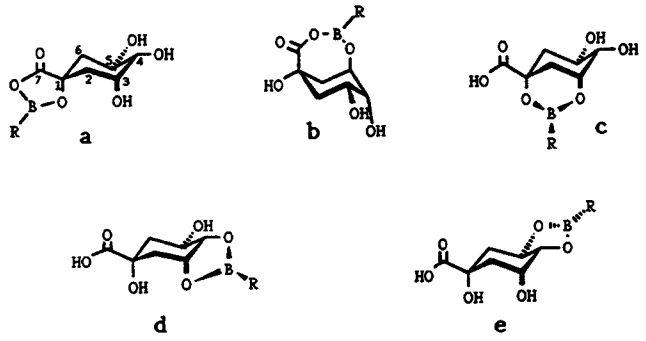

FIGURE 4

tained by selective reaction of the functional groups of quinic acid and reagents at different reaction conditions.

Reactions with BH_3-THF and Phenylboronic Acid. The compounds resulting from the reactions of phenylboronic acid or BH_3 and quinic acid depend on the reaction stoichiometry [3c] and quinic acid protections. Reaction of **1** with one equivalent of BH_3-THF affords the dioxaborolane **21a** in equilibrium with **21b** (doublet at δ +25, J = 173 Hz, in THF). However, with two BH_3 equivalents, a *bis*-dioxaborolane **22** has been isolated (Figure 5). It is interesting that this reaction does not involve reduction of the carbonyl function even at room temperature, as was found in the case of mandelic acid **2**, maybe due to precipitation of compounds **21** or **22** as soon as they are formed. Compounds **21** or **22** have only one ^{11}B NMR signal that denotes that, in each case, the boron atoms are in equilibrium. The assignment of the structures of **21** and **22** was done by comparison with the corresponding phenylboronic derivatives [3c] which were more stable and soluble in $CDCl_3$. Their structures were determined by ^1H NMR, heteronuclear correlations $^{13}C/^1H$, selective irradiation, and $^1H/^1H$ coupling constants. The ^{13}C NMR spectra of compounds **21** present a carbonyl resonance at lower frequency (δ = 173.2) than expected (180 for **21a**). We do not have an explanation for this. It could be attributed to conformational changes or to a solvent effect.

When **21** or **22** is dissolved in DMSO, a ^{11}B NMR signal at δ 9.0 is indicative of a solvent coordination with acidic boron atoms. To date, we have not been able to find an indication of dioxaborolane formation at C-4 and C-5. However, these sites can be coordinated by metal atoms such as Cu [4].

We were interested in exploring quinic acid reactivity when some of its reactive groups are blocked. Therefore, we have prepared derivatives [3c] which have only one free hydroxy group **24** or three free hydroxy groups, **25** and **26** (Figure 5). Lactone **26** was prepared by hydrolysis of **27** which was formed by reaction of quinic acid with phenylboronic acid under acidic conditions [3c]. Compound **24** was synthesized by reaction of quinic acid with 2,2-dimethoxypropane [7]. Basic hydrolysis of dioxolane **24** gave the α-hydroxyacid **25** [3c].

Lactone **26** reacted cleanly and with good yield with BH_3-THF to give the chiral tricyclic dioxaborolane **28** (δ = +27, d, $J \cong$ 160 Hz) (Figure 5). Its structure was also established from ^{13}C NMR by comparison with its carbon analog, the dioxolane **24** [7]. When compound **24** or **28** reacts with BH_3-THF, the boronic hydride **29** or **30**, respectively, is obtained quantitatively. They precipitate from the respective reaction mixtures as white, insoluble moisture sensitive solids. Their ^{11}B NMR resonances in THF-d_8 are characteristic of boronic derivatives (both appear at δ = +27; **30** as a broad signal and **29** as a broad doublet, $J \cong$ 180 Hz). Their ^{13}C NMR spectra were obtained in DMSO-d_6, where both compounds are more soluble (Table 3).

We were interested in testing the reactivity of the quinic acid α-hydroxy acid function when positions C-3 and C-4 were protected. Thus, we found that dioxolane **25** reacts with an excess of BH_3-THF to give a white precipitate soluble only in DMSO. In its ^{11}B NMR spectrum, this reaction product shows a broad resonance at δ +6. The ^{13}C NMR spectrum presents broad signals. The C-1 and C-5 signals were shifted to high frequency, indicative of the formation of a polymeric dioxaborolane with the structure **31a**.

Reactions of Quinic Acid Derivatives with $LiBH_4$. We undertook this study in order to find out how the different functional groups in the quinic acid react to form heterocycles when the boron atom is tetrahedral and nucleophilic. It has been reported that the reaction of **1** with $B(OH)_3$ and KOH in water affords a pair of isomers of spiranic structure **23b** [10] (Figure 5). We have found that the ^{11}B NMR spectrum of the reaction products of **1** with $B(OH)_3$ and KOH in water indicates the presence of two compounds, one resonance at δ +9 and another at +5 assigned to **23b** and to the equilibrium **33a–33b**, respectively. We have carried out the reaction of $LiBH_4$ with two equivalents of **1** in THF and found a similar product **23c** which is soluble in methanol and DMSO. In this reaction, the hydride **32** was also observed as a minor product (5%) (−15.5, d, J = 125 Hz). Compound **23c** presents a similar ^{13}C NMR spectrum to that of compound **23d** [4].

The reaction of an equimolar amount of $LiBH_4$ with quinic acid gave a product that presents a ^{11}B NMR resonance at δ + 4 in CD_3OD. In order to establish whether it has structure **34a** or **34b** (Figure 5), we have analyzed its ^{13}C NMR spectrum. The C-1, C-7, C-3, and C-4 signals are shifted to higher field which clearly shows an equilibrium between both compounds. We have also made dioxolane **25** react with $LiBH_4$ in methanol in 1:1

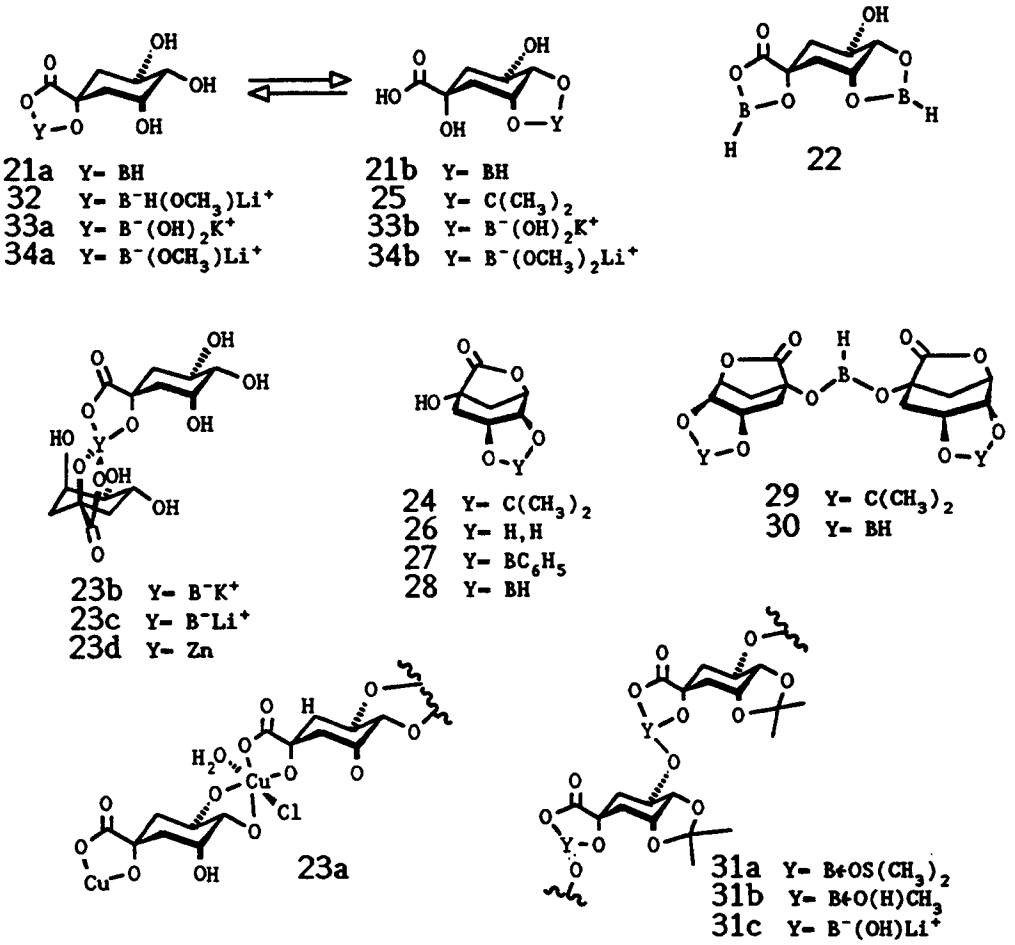

FIGURE 5

and 1:2 ratios, respectively, and in both cases, a very broad signal at δ + 4 [$h_{1/2}$ 600 Hz] indicates the presence of a polymer **31b**.

EXPERIMENTAL

NMR spectra were obtained on a Jeol FX-90 or a Jeol GSX-270 spectrometer. Chemical shifts are reported in δ values, ^{13}C NMR data being referenced to Me_4Si and ^{11}B to BF_3-etherate. The deuterated solvents were dried over molecular sieves prior to use. IR spectra were determined on a Nicolet MX-1 FT spectrometer in KBr. For the preparation of compounds **21–22** and **24–26**, see References 3c and 7. A general procedure for each kind of reaction is reported. The ratio of reagents in each case is indicated in the discussion. All reaction flasks and equipment were dried at 150°C for several hours prior to use and assembled hot under a stream of nitrogen. Special techniques for handling air-sensitive materials were used [11]. The powders were transferred in a glove box in a nitrogen atmosphere, and the liquids were removed by means of syringes provided with long needles. The reagents were purchased from Aldrich. THF was distilled from sodium/benzophenone, 2,3-butanediol was redistilled, and mandelic acid and quinic acid were dried under vacuum. The borane-THF solution was prepared as reported [11]. With the exception of compounds **13**, **14**, and **18**, that are liquids, the other compounds were white powders obtained in quantitative yield. With the exception of compound **9** (mp 116–118°C), **8d** (mp 171–172°C), **10** (mp 128–130°C), and **29** (mp 121–122°C), the reaction products do not melt but decompose above 200°C. They were dissolved in dry deuterated solvents and immediately analyzed by ^{11}B and ^{13}C NMR spectroscopy. The boron compounds could not be isolated as hydrides, owing to their high moisture sensitivity. Their borate derivatives were commonly isolated as solid compounds.

General Procedure for BH_3-THF Reactions

Compound **6**. To a stirred solution of **2** (0.30 g, 1.97 mmol) in dry THF (15 mL), a solution of BH_3-THF 2.3 M (2.57 mL, 5.9 mmol) was added dropwise. After 20 minutes, the solvent was evap-

TABLE 3 ^{13}C and ^{11}B NMR Data [δ, (J, Hz)] and IR (cm^{-1}) of Derivatives of Quinic Acid

	^{13}C NMR								IR	
Compounds	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*^{11}B NMR*	*C=O*	*B–H*
1[a,b,c]	74.5	37.4	69.0	74.5	66.7	40.4	175.6	—	1681	
1[d,e]	75.3	36.4	69.7	74.5	66.0	39.9	177.3	—		
21[b,f]	74.4	34.5	72.1	75.6	67.6	41.3	173.2	+9 s[g]		
22[b,f]	76.3	36.7	73.3	80.2	68.1	40.4	180.5	+9 s[g]		
23c[d,i]	79.3	[j]	69.9	75.5	66.9	[j]	179.8			
	79.5	—	—	75.8	—	—	179.4	+9 (s)[k,l]	1740	
23d[d,h]	77.4	36.8	70.7	75.0	66.8	40.7	180.6	—		
24[d,l,m]	71.4	37.9	71.4	72.0	75.6	34.2	178.9	—		
25[a,b]	71.9	37.3	72.7	78.4	66.6	38.1	180.6	—		
26[a,b,c]	71.4	39.2	65.4	65.1	75.7	37.2	177.5	—		
28[b,d]	70.3	41.3	71.2	71.5	75.1	35.0	177.8	+27 d (160)[n]	1741	2354
29[b,d]	70.6	37.7	71.0	71.7	74.4	34.4	177.9	+27 d (180)[n]	1750	2230
30[b,d]	69.9	40.9	70.1	71.2	74.7	35.0	177.3	+27 d (179)[n]	1741	2344
31a[b,d,o]	76.5	36.1	72.8	80.4	61.4	40.2	181.5	+6 s[b,k]	1732	
33[d,i]	77.3	37.9	72.3	80.6	68.4	41.9	183.0	+5 s[i,k,p]		
34[b,d]	77.3	37.9	72.3	80.6	68.4	41.9	183.0	+4 s[i,k]	1730	

[a]75.43 MHz; [b]DMSO-d_6; [c]ref. 3; [d]67.94 MHz; [e]D_2O; [f]22.52 MHz; [g]**21** appears at +25 ppm' [d, 173], **22** at 30 ppm [d, 168] in THF-d_8; [h]ref. 4; [i]CD_3OD; [j]is not observed; [k]broad signal; [l]$CDCL_3$; [m]isopropyl group: 109.7, 26.9, 24.2 ppm; [n]THF-d_8; [o]isopropyl group: 107.2, 28.2, 25.6 ppm; [p]+9 in D_2O.

orated to leave a white solid (0.32 g, quantitative yield).

Compound **31**c [Y = B^- (OH)Li^+]. Compound **25** (0.30 g, 1.29 mmol) was suspended in dry THF (15 mL), and a solution of BH_3-THF 2.3 M (1.4 mL, 3.44 mmol) was added dropwise. A precipitate formed, and the solvent was evaporated under vacuum. A white solid remained (0.38 g, quantitative yield). Anal. for compound **31** (Y = B-H_2O), $C_{10}H_{12}O_7B \cdot 2B(OH)_3$: calcd. C 31.64, H 5.57; found C 31.17, H 4.76.

Reaction with Phenylboronic Acid

Compound **10.** To a solution of **2** (0.50 g, 3.29 mmol) in dry C_6H_6 (100 mL), phenylboronic acid was added (0.40 g, 3.29 mmol), and the mixture was stirred at reflux with use of a Dean Stark trap during 10 hours. The solvent was evaporated under vacuum, and the residue was a white solid (0.78 g, quantitative yield). Mp 116–118°C. Anal. for compound **10**: $C_{14}H_{11}O_3B$: calcd. C 70.63, H 4.65; found C 69.82, H 4.66.

General Procedure for $LiBH_4$ Reactions

Compound **8c.** To a stirred suspension of $LiBH_4$ (0.043 g, 1.97 mmol) in dry THF (10 mL) a solution of **2** (0.60 g, 3.94 mmol) dissolved in dry THF (15 mL) was added dropwise. The reaction mixture was stirred for 30 minutes at room temperature. The solvent was evaporated under vacuum. The residue was a white solid (0.63 g, quantitative yield). Anal. for compound **8c**, $C_{16}H_{12}O_6BLi \cdot 3H_2O$: calcd. C 51.65, H 4.87; found C 52.08: H 4.83. Anal. for compound **15a**, $C_8H_8O_4BLi \cdot 1.5H_2O$: cald. C 43.48, H 8.67; found C 43.34, H 8.93. Anal. for compound **35**; $C_7H_{10}O_7BLi \cdot 1.5H_2O$: calcd. C 33.50, H 5.22; found C 33.40; H 5.95.

Compound **17.** To a stirred suspension of $LiBH_4$ (0.060 g, 2.63 mmol) in dry THF (40 mL) a solution of **2** (0.40 g, 2.63 mmol) and **3** (0.23 g, 2.63 mmol) dissolved in dry THF (20 mL) was added. A white solid was obtained (0.66 g, quantitative yield). Anal. for compound **17**, $C_{12}H_{14}O_5BLi \cdot 2.5H_2O$: calcd. C 47.88, H 6.36; found C 47.44, H 5.90.

Compound **34.** To a stirred suspension of $LiBH_4$ (0.057 g, 2.60 mmol) in dry THF (40 mL) a suspension of **1** (0.50 g, 2.60 mmol) in dry THF (20 mL) was added. The solvent was evaporated under vacuum. A white solid was obtained (0.62 g, quantitative yield). Anal. for compound **34**, $C_7H_{12}O_8BLi \cdot H_2O$: calcd. C 32.34, H 5.43; found C 32.67, H 5.62.

General Procedure for KOH, $B(OH)_3$ Reactions

Compound **8d.** Compound **2** (0.30 g, 1.97 mmol), $B(OH)_3$ (0.016 g, 0.99 mmol), and KOH (0.05 g, 0.99 mmol) were dissolved in water (5 mL). The reaction mixture was stirred for 30 minutes at room temperature. A white solid was obtained (0.34 g, quantitative yield). Anal. for compound **8d**, $C_{16}H_{12}O_6BK \cdot 0.5H_2O$: calcd. C 53.50, H 3.60; found C 53.48, H 3.7.

Compound **9.** Compound **2** (0.30 g, 1.97 mmol), $B(OH)_3$ (0.032 g, 1.97 mmol), and KOH (0.1 g, 2.0 mmol) were dissolved in water (10 mL). The reaction mixture was stirred for 30 minutes at room temperature. A white solid was obtained (0.46 g, quantitative yield). Anal. for compound **9**, $C_8H_8OB_5K$: calcd. C 41.05, H 3.44; found C 41.52, H 3.27.

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