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Notes

Glass-Catalyzed Conversion of Boronic Esters of Asymmetric Diols to Diol Sulfites and Amine Complexes of Boron Halides

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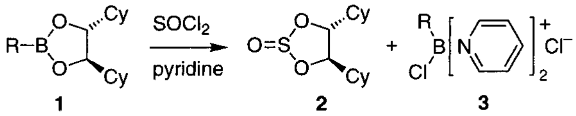
Summary: Sterically hindered boronic esters of (R,R)-1,2-dicyclohexyl-1,2-ethanediol or pinanediol react with thionyl chloride and excess imidazole in acetonitrile on a borosilicate glass surface (but not on silica or soda-lime glass) to form the corresponding cyclic sulfite of the diol and the easily separable organoborane derivative containing one boron-bound chloride and two imidazole groups, which may cross link with additional organoborane moieties to form oligomeric species. Other heterocyclic amines react similarly but usually less efficiently. With excess pyridine, the 1:1 complex $PhBCl_2(py)$ *rapidly forms the 2:1 complex,* $PhBCl(py)_2{}^+Cl^-$*. Hydrolysis of the amino boron chlorides to boronic acids in near neutral aqueous solution provides a mild process for the net hydrolysis of hindered boronic esters, many of which cannot be hydrolyzed by ordinary means, though yields were only 54−82%. The diol sulfites are stable toward water or aqueous acid but rapidly hydrolyzed by base to the diol and inorganic sulfite.*

The utility of boronic esters of chiral diols for the precise control of stereochemistry in asymmetric synthesis is well established.[1] Occasions arise in which it is necessary to hydrolyze or otherwise separate the boronic acid from the diol to which it is esterified, for example, to obtain a boronic acid of biomedical interest,[2] to avoid interference of the diol fragment with subsequent reaction steps,[3] to replace the chiral director with its enantiomer,[4] or to obtain a more reactive organoborane intermediate for use in subsequent reactions.[5] However, hydrolyses of boronic esters of (*R*,*R*)- or (*S*,*S*)-1,2-dialkyl-1,2-ethanediols or pinanediol are thermodynamically disfavored at synthetically useful concentrations of the boronic esters.[3]

Compensation for the thermodynamic barrier has been achieved in several ways. Various means of transesterification in a two-phase system have been used to sequester the desired boronic acid in a separate phase from the diol group.[2−4,6] Sufficiently exothermic ligand transfers can overcome the entropic barrier and lead indirectly to the boronic acid.[5,7,8]

Results

The present investigation began with the discovery that (*R*,*R*)-1,2-dicyclohexyl-1,2-ethanediol ["(*R*)-DICHED"] benzylboronate (**1**, $R = PhCH_2$)[9] reacts with thionyl chloride and excess pyridine to form (*R*)-DICHED sulfite (**2**) and a benzylboron dichloride−pyridine complex, which was later found to contain 2 mol of pyridine (**3**, $R = PhCH_2$). The reaction was faster in acetonitrile than in dichloromethane, and the sulfite ester **2** could be extracted with pentane while the polar boron halide pyridine complex **3** remained in the separate acetonitrile phase. Hydrolysis of **2** to sulfite ion and free DICHED was easily accomplished by treatment with aqueous base. The relatively slow hydrolysis of haloborane complex **3** to benzylboronic acid with water in acetonitrile-d_3 was found by NMR to follow good pseudo-first-order kinetics.



The model system worked very well, as indicated by the complete disappearance of the characteristic multiplet at δ 3.82 (2H, C*H*OB) in the 300 MHz ^{1}H NMR spectrum of DICHED boronate **1** ($R = PhCH_2$) and the overnight appearance of the corresponding diastereotopic pair of protons of sulfite ester **2** as two double doublets at δ 4.07 and 4.58 (2H, C*H*OS). A number of

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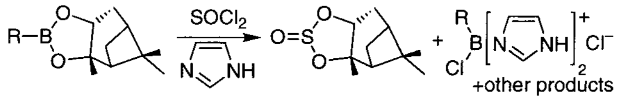
other DICHED boronic esters **1** were screened by NMR and generally found to react similarly, though reactions were often incomplete. Imidazole was found to react faster than pyridine as the amine component.

The more hindered pinanediol phenylboronate **4** (R = Ph; C*H*OB δ 4.45) was inert to thionyl chloride and pyridine but with imidazole was partially converted to pinanediol sulfites **5** (diastereomeric pair, δ 4.72 and 4.94) and a phenylboron chloride imidazole derivative **6** in a mixture with analogous, more complex products.



4 **5** **6**

Glass Surface Catalysis. Our initial success came unraveled when a new investigator attempted to define practical process conditions. No reaction at all occurred when **1** (R = PhCH$_2$) was treated with thionyl chloride from a fresh bottle in anhydrous acetonitrile in a clean new flask and either anhydrous pyridine or imidazole!

Subsequently, older samples of thionyl chloride with imidazole produced small conversions of **1** to sulfite ester **2**. Reactions would proceed part way within a few hours and then stop at some erratic final conversion. With a recent case of catalysis by a reagent impurity in mind,[10] we tested small amounts of several additives to the thionyl chloride, including water, sulfuryl chloride, chlorosulfonic acid, azobis(isobutyronitrile), disulfur dichloride, titanium trichloride, and ferrous chloride. None of these produced any consistent effect. For example, triplicate reactions in the presence of excess imidazole and a small amount of ferrous chloride produced random conversions of 91, 10, and 15%.

The mystery was solved after Professor D. C. Dittmer suggested glass surface catalysis, with which he had had previous experience.[11] Addition of borosilicate glass powder (0.1−1 mm particles, 5 times the weight of **1**) to the reaction mixture of **1** (R = PhCH$_2$) with pyridine and thionyl chloride resulted in 65% conversion to **2** after 17 h at room temperature. Pyridine and **1** consistently failed to react at all with thionyl chloride in the absence of a catalyst, and silica gel led to only 5% conversion. Evidently the first investigator was able to discover the reaction because he routinely cleaned his glassware with alcoholic potassium hydroxide and thus was working with well-etched glass surfaces. As the new flasks used by the second investigator became scratched, his reactions began to proceed.

Reactions of DICHED boronic esters **1** with thionyl chloride do not occur at all in the absence of a heterocyclic amine. Reactions involving DICHED esters and imidazole are often virtually complete within a few minutes at room temperature. To get complete conversion, at least 4 mol of imidazole are required. Characteristically, if reactions are not complete within an hour, stirring the mixture for another day or two produces only a few percent of additional conversion, as if the glass surface becomes coated with the reaction products and consequently inactivated. Glass added after the reaction has stopped will catalyze only a small amount of further reaction. Reactions involving pyridine and DICHED esters are considerably slower, to the point that they may not go to completion if a (*sec*-alkyl)boronic ester is involved. Other bases such as *N*-methylimidazole and pyrazole also react but have not been tested extensively. Typical conversions of DICHED boronic esters measured by ^{1}H NMR are summarized in Table 1.

Table 1. Conversions of (*R*)-DICHED Boronic Esters (1) to (*R*)-DICHED Sulfite (2) and Organoboron Chloride Complexes with Amines (3, 6, or Others)

R of **1**	amine[a]	*t* (h)	*T* (°C)	**2** (%)
Ph	im[a]	1.5	22	95
Ph	py[a]	24	55	67
Ph	py	200	55	98
Ph	bipy[a]	170	55	77
PhCH$_2$	im	0.5	22	99
PhCH$_2$	py	24	22	98
PhCH$_2$	Me-im[a]	20	22	81
PhCH$_2$	pyzl[a]	18	22	21
PhCH$_2$	pyzl	48	22	80
(*S*)-PhCH$_2$CH(CH$_3$)	im	4	22	99
(*R*)-PhCH$_2$CH(OCH$_2$Ph)	im	24	22	99
(*R*)-PhCH$_2$CH(*c*-C$_6$H$_{11}$)	im	100	65	16
(*R*)-PhCH$_2$CH(Cl)	im	0.5	22	99
(*R*)-(*c*-C$_6$H$_{11}$)CH(CH$_3$)[b]	im	24	22	68
(*R*)-CH$_3$CH(OCH$_2$Ph)[b]	im	24	22	99

[a] Amines: im, imidazole; py, pyridine; bipy, 2,2′-dipyridyl; Me-im, *N*-methylimidazole; pyzl, pyrazole. [b] Enantiomer of this compound was used.

Reactions of pinanediol esters (**4**) usually fail with pyridine and are sluggish with imidazole. There is usually an induction period of a few hours before a significant amount of reaction occurs. Only partial cleavage of pinanediol esters has been achieved when the boron bears a *sec*-alkyl substituent. Pinanediol esters provide a particularly sensitive test of catalyst effectiveness, and soda-lime glass as well as silica proved inactive. Results with and without added crushed borosilicate glass are summarized in the Supporting Information.

MALDI mass spectroscopic analysis of the imidazole−chloroborane adducts showed molecular fragments containing alkylborane and imidazole units in ratios of 1 to 2, corresponding to the cation of **6**. Higher molecular weight species were also present, indicating bridging of an imidazole unit between two boron atoms, with the species having 2 boranes to 3 imidazoles being prominent. Ions from the pyridine derivatives contained 1 or 2 pyridines, and bipyridyl showed only the 1:1 adduct. Details of the MALDI spectra are summarized in the Supporting Information.

Although we had no difficulty preparing an analytically pure sample of the known 1:1 adduct of phenylboron dichloride with pyridine, we were unable to obtain the 1:2 adduct in satisfactory analytical purity in several attempts. NMR evidence indicated that the 1:1 adduct is converted to a 1:2 adduct as soon as more than 1 equiv of pyridine is added. 2,2′-Dipyridyl yields a 1:1 adduct with phenylboron dichloride. The inherent complexity of the imidazole system discouraged any attempt to isolate its components.

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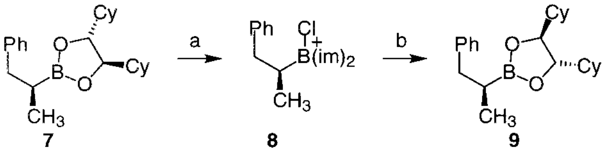
(11) (a) Dittmer, D. C.; Marcantonio, A. F. *J. Org. Chem.* **1964**, *29*, 3473−3475. (b) (α-Chloroallylic)boronic esters, which can be useful synthetic intermediates, are in some cases difficult to make and to substitute.[1b] Allylic isomerization on glass surfaces as described by Dittmer and Marcantonio is a likely side reaction that has been overlooked.

Recovery of Boronic Acid and Diol. Diol recovery from the sulfite ester is simple and quantitative. DICHED sulfite (**2**) is stable to aqueous acid or neutral water but very rapidly hydrolyzed by aqueous base. Extraction with pentane leaves the polar organoboron dichloride amine adducts in the acetonitrile phase and extracts **2** into the pentane phase, together with any unchanged boronic ester. Separation of the polar and nonpolar products is sometimes more efficient if some water is added, provided the aqueous acetonitrile phase is kept acidic to prevent hydrolysis of the diol sulfite.

The organoboron dichloride imidazole adducts are more resistant to hydrolysis. The overall yield of phenylboronic acid from (*S*,*S*)-DICHED phenylboronate (***ent*-1**, R = Ph) via refluxing crude **6** (R = Ph) in aqueous acetonitrile was 82%. Similar treatment of other **1** or ***ent*-1** (R = $PhCH_2$, $PhCH_2CH(OBn)$, $PhCH_2$-CH(Me), cyclohexyl) yielded 54−69% of the corresponding boronic acids.

Boronic acids are hard to purify, and to get a representative accurate yield as well as demonstrate a potential use of the process, the (*R*)-(+)-DICHED ester **7** was cleaved with thionyl chloride and imidazole. The resulting mixture of haloborane amine complex **8** and related compounds was hydrolyzed and treated with (*S*,*S*)-DICHED to form (−)-**9**, 56% after chromatography. The diastereomers **7** and **9** showed small differences in chemical shifts in the ^{13}C NMR spectra, and no **7** was detected in **9** at a signal-to-noise ratio of 200:1.



7 **8** **9**

(a) $SOCl_2$, imidazole, crushed glass, 20-25 °C, 24 h.
(b) H_2O/MeOH, reflux; (*S*,*S*)-DICHED.

Discussion

Glass Catalysis. Glass surface catalyzed reactions are reported sporadically, but usually involve a nonpolar medium in contact with the polar surface, as in the ionic equilibration of crotyl and methallyl chlorides.[11] Glass-catalyzed fluorinations by xenon difluoride, presumably via XeF^+, are inhibited by acetonitrile.[12] Polar solvents diminish catalysis of Diels−Alder reactions by silica or glass.[13] Isotopic O-exchange between sulfate, phosphate, or chromate and strongly basic water is apparently catalyzed by silicate etched from the glass rather than the surface itself.[14] Other miscellaneous examples of surface catalysis show a wide variety of behavior.[15]

The specific activity of borosilicate glass and the failure of silica to catalyze these boronic ester reactions appears to be a unique phenomenon. Ordinarily the catalytic activities of silica and glass are comparable and may be attributed to hydroxyl groups on the surfaces. Glass, quartz, or silica surfaces are covered with Si−OH groups at an estimated packing density ~4.7/100 $Å^2$.[16] It is plausible that a boronic ester bound diol might exchange to a tricoordinate boron oxide/hydroxide site in the glass, perhaps to form a tetracoordinate borate site, but that silica sites do not provide a thermodynamically competitive possibility for binding to diols.

Boron Halide Amine Adducts. Most reports of reactions of amines with alkylboron dichlorides have described 1:1 adducts. A computer search of *Chemical Abstracts* for compounds containing the tetracoordinate boron grouping $CBCl_2N$ yielded 21 citations, all in the period 1943−1981. A search for $CBClN_2$ structures produced only two, not including $MeB(Cl)(NHMe_2)_2{}^+Cl^-$,[17] found via the report of $CF_3B(Cl)(NHMe_2)_2{}^+Cl^-$.[18] The 1:1 adduct of pyridine with phenylboron dichloride, $PhBCl_2(py)$, has been described.[19]

A closer analogy to the chemistry reported here is the reaction of aminodichloroboranes with 2 or 3 mol of pyridine, as in the conversion of Me_2NBCl_2 to the 1:2 adduct $Me_2NBCl(py)_2{}^+Cl^-$ and of Et_2NBCl_2 to $Et_2NB(py)_3{}^{2+}\cdot 2Cl^-$.[20] In other work, the possibility that organoboron dichlorides might react with more than 1 equiv of amine has been overlooked.[21]

Another precedent for reaction of more than one amine is provided by tris(pyrazolyl)borates ("pyrazaboles"),[22] especially their stepwise synthesis from organoboron halide precursors,[23] though no evidence for tris(amino)alkylborates was seen in the present work. Nucleophilic substitutions at tetracoordinate boron are known to proceed either via direct "S_N2" displacements or "S_N1" dissociation to tricoordinate boron intermediates.[24]

The molecular masses indicated by MALDI data are consistent with the type and variety of organoboron dichloride imidazole adducts that would be expected. The stoichiometry of formation of cations containing bridging imidazole units requires formation of an equivalent amount of imidazole hydrochloride, in accord with observations that complete conversion of boronic esters to their imidazole boron dichloride derivatives requires at least 4 equiv of imidazole and works better with 5 or 6.

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Experimental Section

Reaction of DICHED Boronic Esters (1) with Imidazole and Thionyl Chloride. Crushed borosilicate glass (particle size ∼0.1−1 mm) was cleaned with hydrochloric acid, treated with methanolic potassium hydroxide for several hours, washed thoroughly with deionized water, and dried in an oven. Imidazole was dried under vacuum (1 Torr) at 20−25 °C for 1−2 days. The DICHED boronic ester (**1**) (0.5 mmol, 150−200 mg) and imidazole (136 mg, 2.0 mmol) were dissolved in anhydrous acetonitrile (2.5 mL) under an inert atmosphere (argon) with the aid of a magnetic stirrer. After the imidazole had dissolved, crushed borosilicate glass (1 g) was added. Thionyl chloride (360 mg, 3 mmol) was added dropwise, and vigorous stirring was continued. After the time indicated in Table 1, the reaction mixture was filtered (suction). The acetonitrile solution was extracted with pentane (3 × 5 mL). Concentration of the pentane phase yielded DICHED sulfite (**2**) and any unchanged boronic ester (**1**), the ratio of which was determined by comparison of the integrals of the 300 MHz ^{1}H NMR signals of **1** near δ 3.8 and the corresponding diastereotopic pair of signals of DICHED sulfite at δ 4.05 and 4.56. Concentration of the acetonitrile phase yielded a mixture of boron chloride imidazole complexes (**6** and related oligomers).

Reaction of DICHED Boronic Esters with Pyridine and Thionyl Chloride. The procedure was the same as that described for reactions with imidazole, but with the following modifications. Boronic ester **1** (0.5 mmol) in acetonitrile (2.5 mL) was stirred with crushed borosilicate glass (1 g) during the dropwise addition of thionyl chloride (120 mg, 1 mmol) followed by the dropwise addition of pyridine (200 mg, 2.5 mmol).

[2(1*R*),4*R*,5*R*]-4,5-Dicyclohexyl-2-(1-methyl-2-phenylethyl)-1,3,2-dioxaborolane (9) from [2(1*R*),4*S*,5*S*]-4,5-Dicyclohexyl-2-(1-methyl-2-phenylethyl)-1,3,2-dioxaborolane (7). A slurry of crushed borosilicate glass (10 g, pretreated as described above) in a solution of anhydrous imidazole (3.65 g, 53.6 mmol) and (*R*)-DICHED ester **7** (1.9 g, 5.37 mmol; $[\alpha]^{22}_{D}$ +29.2°, $[\alpha]^{22}_{546}$ +35.6° (c 0.24, CH_2Cl_2)) in anhydrous acetonitrile (130 mL) was stirred under argon during the dropwise addition of thionyl chloride (5.87 mL, 80.5 mmol) and stirred for an additional 24 h at 20−25 °C. NMR analysis of an aliquot indicated >98% conversion of **7** to DICHED sulfite. Water was added until the yellow organic solid was dissolved, leaving the solid (glass) phase colorless. The aqueous acetonitrile phase was extracted with pentane (5 × 150 mL) to remove DICHED sulfite and unconverted boronic ester. The acetonitrile solution was concentrated on a rotary evaporator. A mixture of water (50 mL) and methanol (150 mL) was added until the granular tan yellow solid dissolved. The mixture was refluxed for 15 h. After cooling to room temperature, (*S*,*S*)-DICHED (1.34 g, 5.93 mmol) was added to the boronic acid solution. The solution was stirred at 60 °C overnight. Methanol was evaporated by a rotary evaporator, and ether (150 mL) was added to the granular tan solid. The mixture was shaken and separated, and the extraction with ether was repeated (3 × 150 mL). The ether phase was dried over magnesium sulfate and concentrated in a rotary evaporator. Analytically pure compound was obtained by flash chromatography on silica with ether/pentane (1:20) (1.07 g, 56.4%): $R_f = 0.5$ (silica gel 5% ether in pentane); oil, $[\alpha]^{22}_{D}$ −37.7°, $[\alpha]^{22}_{546} = -44.6°$ (c 0.79, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83−1.75 (m, 26H), 2.56 (dd, J = 13.5 Hz, J = 8.4 Hz, 1H), 2.83 (dd, J = 13.2 Hz, J = 7.2 Hz, 1H), 3.80 (d, J = 4.5 Hz, 2H), 7.1−7.3 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 25.9, 26.0, 26.5, 27.3, 28.2, 39.3, 42.9, 83.2, 125.4, 127.8, 128.7, 142.1; HRMS calcd for $C_{23}H_{25}BO_2$ 354.2730, found 354.2727. Anal. Calcd for $C_{23}H_{25}BO_2$: C, 77.95; H, 9.96; B, 3.05. Found: C, 78.25; H, 10.23; B, 2.75.

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Supporting Information Available: Data for reactions with and without added glass; preparation and characterization data for **1** or ***ent*-1** [R = Ph, *n*-hexyl, cyclohexyl, $PhCH_2CH(CH_3)$, $PhCH_2CH(C_6H_{11})$, $PhCH_2CH(OCH_2Ph)$, $CH_3CH(C_6H_{11})$, $H_2C{=}CH{-}CH_2CH(CH_3)$], cyclohexylboronic acid, (*S*)-(1-phenylmethoxy-2-phenylethyl)boronic acid, pinacol esters of (1-methyl-2-phenylethyl)boronic acid and (1-benzyloxy-2-phenylethyl)boronic acid, (*R*)-DICHED sulfite (**2**), pinanediol sulfites (**5**); hydrolysis of imidazole borates **6** to boronic acids; summary of MALDI-TOF measurements; rate of hydrolysis of pyridine adduct of benzylboron dichloride; ^{1}H and ^{13}C NMR curves for compounds **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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