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A Comparative Study of the Relative Stability of Representative Chiral and Achiral Boronic Esters Employing Transesterification

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Summary. A comparative study of the transesterification of five representative chiral and achiral boronic esters with various structurally modified diols was undertaken to qualitatively understand the factors influencing the relative stability of these boronic esters. Several factors such as chelation, conformation, steric bulk of the substituents, size of the heterocycle, and entropy influence the relative rate of transesterification as well as the stability of the boronic esters. Amongst these boronic esters, pinanediol phenylboronic ester was found to be the most stable boronic ester whereas *DIPT* boronic ester appeared to be thermodynamically the least stable one. The transesterification with sterically hindered diols was observed to be relatively slow, but afforded thermodynamically more stable boronic esters. Boronic esters derived from *cis*-cyclopentanediols and the bicyclo[2.2.1]heptane-*exo*,*exo*-2,3-diols are relatively more stable. This study not only presents the qualitative picture of relative stability of various boronic esters, but also provides helpful hints regarding the possible recovery of chiral auxiliaries. Many C_2-symmetric chiral auxiliaries, such as 2,3-butanediol, 2,4-pentanediol, *DIPT*, and *cis*-cyclohexane-1,2-diol, can be retrieved by simple transesterification of the corresponding boronic esters with commercial inexpensive diols, such as pinacol, 1,3-propanediol, and neopentyl glycol.

Keywords. Boronic esters; Diols; Transesterification; Chiral auxiliaries.

Introduction

The usefulness of boronic acids and their esters in synthetic and biomolecular chemistry is well recognized over the last decade [1]. Some of the biomolecular applications include their uses in serine proteases inhibition [2], transmembrane transport [3], separation of glycoproteins [4], boron neutron capture therapy (BNCT) [5], as a glucose-selective fluorescence sensor [6], as drug delivery agents [7], and as a redox-sensitive protecting group [8]. In synthetic organic chemistry, they have been used extensively in the *Suzuki* coupling reactions [9], *Petasis* reactions [10], copper and rhodium catalyzed cross-coupling reactions [11], *Diels-Alder* reactions [12], *Matteson*'s asymmetric homologation reactions [13], annulation reactions [14], asymmetric synthesis of amino acids [15], and separation of cyclic *cis*- and *trans*-stereoisomeric 1,2-diols [16]. Boronic esters are also valuable compounds as protecting groups in carbohydrate chemistry [17], as chiral derivatizing agents [18], as chiral auxiliaries [19], and as precursors to boron enolates [20].

The stability of the boronic esters plays a key role in chiral auxiliary directed multistep organic synthesis. *Matteson et al.* achieved a very high degree of stereo- and enantioselectivities (>99% *ee*) during the successive one-carbon homologation of cyclic boronic esters derived from pinanediol with preformed (dichloromethyl)lithium [13, 21]. The recovery of the chiral auxiliary, pinanediol, became a difficult task

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† This paper is dedicated to the memory of my mentor, the late Professor *Herbert C. Brown* (1912–2004). Professor *Herbert C. Brown* deceased on December 19, 2004. The work described herein was carried out at Purdue University during my stay as a post-doctoral research associate

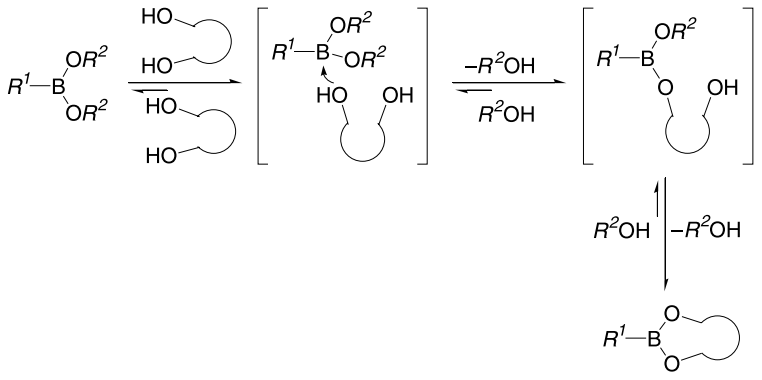

Fig. 1. An entropically-favored diol exchange of the acyclic boronate with a cyclic diol

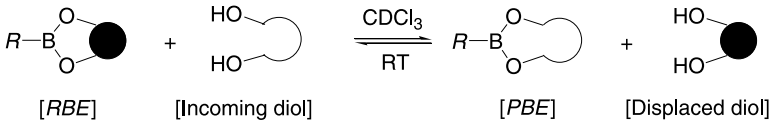

Fig. 2. A generic scheme for transesterification

due to the unusual stability of pinanediol boronic esters toward ligand exchange or hydrolysis. Later, *Brown et al.* succeeded in developing several procedures for the recovery of pinanediol from pinanediol boronic esters [22, 23]. In order to introduce a new stereogenic center of desired configuration in *Matteson*'s asymmetric homologation, the requirement for the removal of the first chiral diol and replacement by its enantiomer or some other chiral auxiliary, was well recognized during the synthesis of stegobinone [24]. Transesterification can prove to be a very easy avenue to introduce as well as retrieve the chiral auxiliaries to or from boronic esters in a very efficient manner, provided the final boronic ester is thermodynamically more stable than the starting boronic ester. Recently we reported the structural effects on the relative rates of transesterification of 2-phenyl[1,3,2]dioxaborolane [25a] and pinanediol methylboronic ester [25b] as well as the stereoisomer-differentiating esterification of diols with methylboronic acid (separation of *cis*,*trans*-1,2-diols) [25c].

Ligand exchange reactions are greatly influenced by various factors, such as chelation, conformation, entropy, catalyst, solvent polarity, and concentration, the entropies of internal rotations of free diols and the steric repulsions on enthalpy appear to be the dominant factors in transesterification or hydrolytic cleavage of boronic esters, as described by *Matteson* and *Man* [24]. Acyclic boronic esters undergo rapid hydrolysis or transesterification in comparison with their cyclic analogs. The energetics of such reactions are favored by an increase in entropy (two moles of reactants converting into three moles of products) as well as an intramolecular nucleophilic attack (lower activation energy pathway) in the second step by the cyclic diol (Fig. 1).

In the present study, the temperature and the solvent are unlikely to affect the transesterification for obvious reasons. In the hope of further understanding the factors influencing the relative stability of boronic esters, we undertook a general study of transesterification of five representative chiral and achiral boronic esters **1**–**5** with various commercial as well as synthesized structurally modified diols. In this report, we present our qualitative results on the relative stability of a large set of boronic esters by ^{1}H NMR employing transesterification protocol (Fig. 2).

Results and Discussion

For comparative study, two chiral boronic esters **1**–**2** and three achiral boronic esters **3**–**5** were prepared by esterification of phenylboronic acid with the corresponding diols in *n*-pentane in 4–6 h at room temperature in excellent chemical yields (75–85%) and purity (Fig. 3) [26]. Various structurally-varied diols were synthesized by OsO_4-catalysed *cis*-dihydroxylation of the corresponding olefins in

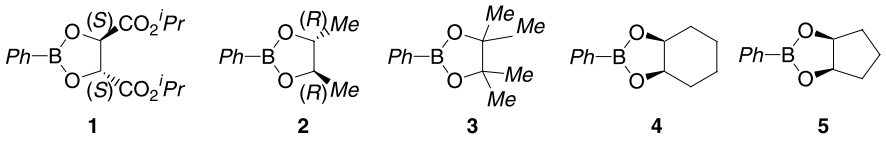

Fig. 3. Representative chiral and achiral boronic esters **1**–**5**

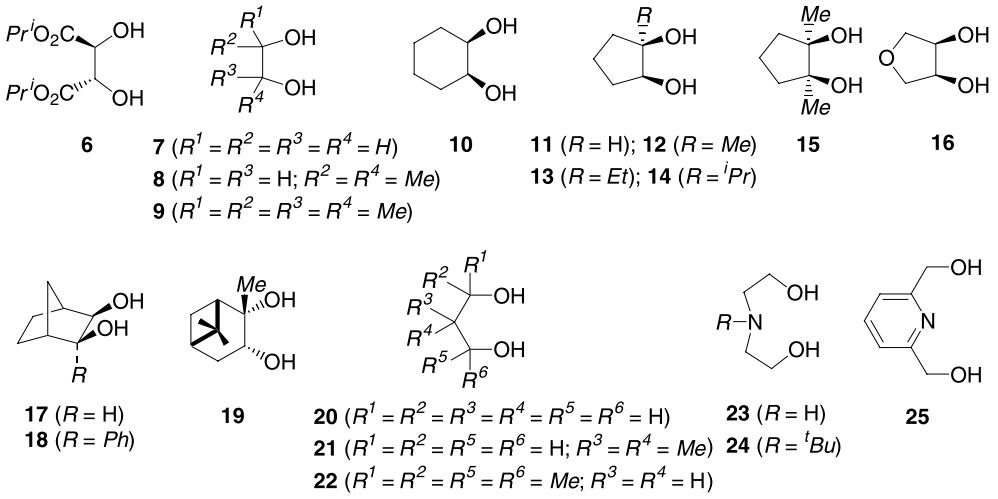

Fig. 4. Various commercial and synthesized diols **6**–**25**

>75% yields (Fig. 4) [27]. It is well known that the equilibrium composition is highly solvent dependent, the solvent, $CDCl_3$ was chosen in the present study. Transesterification was carried out in an NMR tube (0.05 mmol of both boronic ester and diol in 1 cm^3 $CDCl_3$) under nitrogen at RT and the progress of the exchange reaction was monitored by ^1H NMR spectroscopy. The $CDCl_3$ (same solvent batch) used for this study was stored over molecular sieves. With several boronic esters, the equilibrium measurements were carried out by approaching equilibrium from both directions of reaction. Initially, all the reactions were monitored very frequently (every 5–15 min) soon after mixing. In the cases of very slow reactions, the time intervals for monitoring the reactions were extended to 12–24 h (based on extent of initial exchange). In all the experiments, the disappearance and an appearance of characteristic ^1H peaks were monitored until there were no more changes in product formation (reaching equilibrium).

Table 1. Transesterification of chiral (+)-diisopropyl (*L*)-tartrate phenylboronic ester (**1**) with representative diols in $CDCl_3$

Entry	Diol	Time/h	Equilibrium compositions *RBE* (%) ⇌ *PBE* (%)
1	Ethylene glycol **7**	0.1	01 ⇌ 99
2	(+)-2,3-Butanediol **8**	0.1	02 ⇌ 98
3	Pinacol **9**	48	01 ⇌ 99
4	*cis*-1,2-Cyclohexanediol **10**	20	08 ⇌ 92
5	*cis*-1,2-Cyclopentanediol **11**	0.25	01 ⇌ 99
6	α-Pinanediol **19**	0.25	01 ⇌ 99
7	1,3-Propanediol **20**	0.1	01 ⇌ 99
8	2,2-Dimethyl-1,3-propanediol **21**	0.1	01 ⇌ 99
9	2,4-Dimethyl-2,4-pentanediol **22**	3	01 ⇌ 99
10	Diethanolamine **23**	0.1	01 ⇌ 99
11	*N-tert*-Butyldiethanolamine **24**	0.1	01 ⇌ 99
12	2,6-Pyridinedimethanol **25**	0.1	10 ⇌ 90

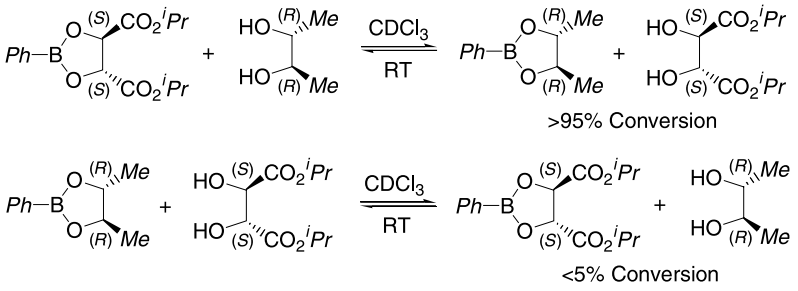

Fig. 5. Transesterification of boronic ester **1**

*Transesterification of Chiral (+)-2-Phenyl[1,3,2]-dioxaborolane-4,5-dicarboxylic Acid Diisopropyl Ester (**1**)*

The chiral auxiliary, (+)-diisopropyl tartrate (*DIPT*) has been a very useful chiral director in synthesis, especially in the boronic ester based asymmetric allenylboration [28, 29], allylboration [30] and crotylboration [31]. The recovery of the costly chiral auxiliary from the boronic ester becomes an important task in the chiral auxiliary directed asymmetric synthesis. Therefore, it was of interest to examine the thermodynamic stability of the (+)-diisopropyl (*L*)-tartrate phenylboronic ester **1**. It is quite obvious from Table 1 that the (+)-diisopropyl (*L*)-tartrate phenylboronic ester is the least stable boronic ester (Fig. 5). Except for diols **9** and **10**, all the diols instantaneously displaced *DIPT*. Such facile ligand exchange may possibly be due to minimal steric repulsions between the 4,5-substituents in new product boronic esters (as compared to *trans*-4,5-diisopropyl carboxylate groups in **1**). The slow transesterification with pinacol **9** may be attributed to the steric factor. The chiral auxiliary, *DIPT* can easily be recovered by conducting the reaction in *n*-pentane [25c]. The resulting boronic esters are usually soluble in *n*-pentane whereas decanting the *n*-pentane layer easily retrieves the displaced insoluble diol.

*Transesterification of Chiral (−)-4,5-Dimethyl-2-phenyl[1,3,2]dioxaborolane (**2**)*

(*R*,*R*)-(−)-2,3-Butanediol has also been used as an effective C_2-symmetric chiral auxiliary in asymmetric synthesis, especially in *Matteson*'s asymmetric homologation [21b]. The boronic ester **2** is also an ideal substrate for studying and comparing the thermodynamic stability gained by the boronic esters due to the size and structure of the ring. Therefore, it was of considerable interest to examine the transesterification of the boronic ester **2**. It was interesting to compare the extent of transesterification with the *cis*-1,2-cyclohexanediol **10** and the *cis*-1,2-cyclopentanediol **11**, since both are very similar to 2,3-butanediol (4,5-disubstituted borolane, except for the cyclic structure). Again, the favorable equilibrium for the boronic ester **5** over the boronic ester **4** (entries 3 and 4) clearly demonstrates the significance of coplanarity while evaluating the stability of the cyclic

Table 2. Transesterification of (−)-(phenyl)-1,3,2-dioxa-4,5-dimethylborolane (**2**) with representative diols in $CDCl_3$

Entry	Diol	Time/h	Equilibrium compositions *RBE* (%) ⇌ *PBE* (%)
1	(+)-Diisopropyl (*L*)-tartrate **6**	0.1	95 ⇌ 05
2	Pinacol **9**	302	37 ⇌ 63
3	*cis*-1,2-Cyclohexanediol **10**	5.75	86 ⇌ 14
4	*cis*-1,2-Cyclopentanediol **11**	20	14 ⇌ 86
5	α-Pinanediol **19**	2.5	08 ⇌ 92
6	1,3-Propanediol **20**	0.3	49 ⇌ 51
7	2,2-Dimethyl-1,3-propanediol **21**	0.75	29 ⇌ 71
8	2,4-Dimethyl-2,4-pentanediol **22**	258	20 ⇌ 80
9	Diethanolamine **23**	0.15	70 ⇌ 30

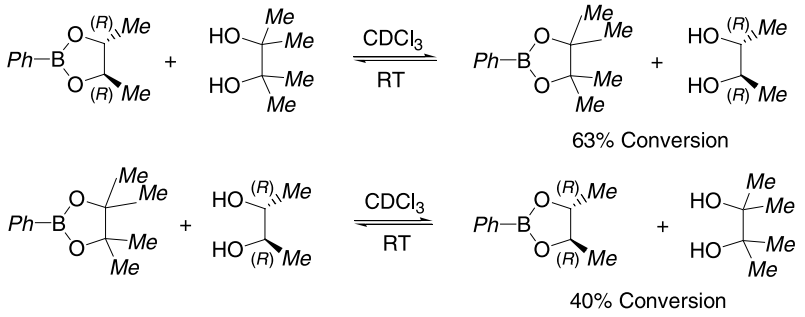

Fig. 6. Transesterification of boronic ester **2**

boronic esters (Table 2). In general, the formation of bicyclic structures are entropically favored over monocyclic ones. As expected, the steric factor slows down the exchange reaction between boronic ester **2** and the pinacol, but produces the thermodynamic equilibrium composition favoring tetrasubstituted pinacolyl boronic ester **3** (60–63%) over the disubstituted boronic ester **2** (Fig. 6). Although, diethanolamine was highly effective with boronic ester **1**, only 30% transesterification was observed with boronic ester **2**. Again, the 4,6-disubstituted borinane (entry 8) is relatively more stable than the unsubstituted borinane (entry 6).

*Transesterification of 4,4,5,5-Tetramethyl-2-phenyl-[1,3,2]dioxaborolane (**3**)*

Pinacolyl boronic esters have found wide applications in cross-coupling chemistry. Unlike other boronic esters (except for pinanediol boronic esters), pinacolyl boronic esters are generally very stable and can be purified by silica gel column chromatography. Deprotection of pinacol from their boronic esters has been achieved using diethanolamine/HCl [32] and KHF_2/base [33]. *Pennington et al.* [34] successfully deprotected the pinacolyl boronic esters by transesterification with polystyrene-boronic acid. To compare the relative stability of pinacolyl boronic ester, ligand exchange of boronic ester **3** was carried out with a series of diols. Amongst the various diols studied, the highly effective diol (except for pinanediol) appeared to be the *exo*,*exo*-norbornanediol **17** (entry 3). The rate of exchange was also relatively faster than for other diols. The easy transesterification of pinacolyl boronic ester with 1,2-diisopropylethanediol or 1,2-dicyclohexylethanediol clearly suggests that the steric repulsions between the methyl groups destabilize five-membered pinacolyl boronic ester [24]. Such repulsive interactions are minimal in norbornanediol boronic esters. The unusually slow ligand exchange of **3** with pinanediol **19** (entry 4) is mainly attributed to the orientation and the rigidity of the free diol. It was surprising to observe the ineffectiveness of diethanolamine **23** (entry 7) taking into account that the nitrogen atom of the diethanolamine had the ability to provide an additional stability to the boronic ester by chelation. In contrast, the *DIPT* boronic ester **1** underwent quantitative transesterification with **23**, under identical conditions in $CDCl_3$ in <5 min (Table 1, entry 10). Transesterification with diethanolamine is known to be highly efficient but in nonhalogenated solvents as the driving force is taken

Table 3. Transesterification of 4,4,5,5-tetramethyl-2-phenyl[1,3,2]dioxaborolane (**3**) with representative diols in $CDCl_3$

Entry	Diol	Time/h	Equilibrium compositions *RBE* (%) ⇋ *PBE* (%)
1	(+)-2,3-Butanediol **8**	270	60 ⇌ 40
2	*cis*-1,2-Cyclopentanediol **11**	291	20 ⇌ 80
3	*exo*,*exo*-2,3-Norbornanediol **17**	92	04 ⇌ 96
4	α-Pinanediol **19**	764	04 ⇌ 96
5	1,3-Propanediol **20**	888	55 ⇌ 45
6	2,2-Dimethyl-1,3-propanediol **21**	894	47 ⇌ 53
7	Diethanolamine **23**	21	88 ⇌ 12

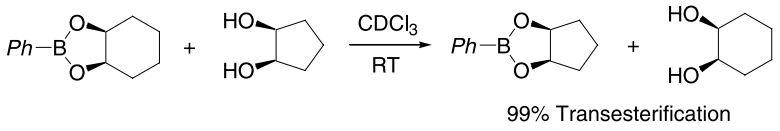

Fig. 7. Transesterification of boronic ester **4**

to be the precipitation of the diethanolamine adduct. The results are tabulated in Table 3.

*Transesterification of 2-Phenylhexahydrobenzo-[1,3,2]dioxaborole (**4**)*

To understand the effect of ring size fused with [1,3,2]dioxaborolane on the thermodynamic stability, the transesterification of the boronic ester **4** was studied with few representative diols. The quantitative displacement of *cis*-1,2-cyclohexanediol from its boronic ester by *cis*-1,2-cyclopentanediol unambiguously establishes that the boronic ester **5** is much more stable than the boronic ester **4** (Fig. 7, Table 3). The conversion of higher energy boat conformation (partial inversion of the chair-form diol to the boat form to attain coplanarity for an intramolecular transesterification) of boronic ester **4** into the boronic ester **5** which is a lower energy planar boat conformation, is most likely the driving force. The boronic ester **4** underwent quantitative diol exchange with all the three cyclopentane-based diols (entries 1–3) which suggests that C_2-symmetric chiral *cis*-1,2-cyclohexanediol can be retrieved from its boronic ester using these cheap diols.

*Transesterification of 2-Phenyltetrahydrocyclopenta-[1,3,2]dioxaborole (**5**)*

A qualitative picture of an additional thermodynamic stability gained due to the cyclic structure of the diol can be obtained by transesterification of the boronic ester **2** with diols **10** and **11**. The equilibrium composition favoring the boronic ester **5** (86%) in comparison with the boronic ester **4** (14%) clearly establishes that the boronic ester **5** is thermodynamically much more stable than the boronic ester **4** (Fig. 8). Since the formation of the cyclic boronic ester requires a coplanar intermediate, such difference in stability can be interpreted in terms of conformational factors. The carbon-oxygen bonds in the *cis*-cyclopentane-1,2-diol (boat form) are essentially coplanar (dihedral angle nearly 0°) whereas the *cis*-cyclohexane-1,2-diol is chair-shaped and the carbon-oxygen bonds make a dihedral angle of approximately 60°. The partial inversion of the chair-form into the

Table 4. Transesterification of 2-phenylhexahydrobenzo[1,3,2]dioxaborole (**4**) with representative diols in $CDCl_3$

Entry	Diol	Time/h	Equilibrium compositions *RBE* (%) ⇌ *PBE* (%)
1	1,4-Anhydroerythritol **15**	0.5	01 ⇌ 99
2	*cis*-1,2-Cyclopentandiol **10**	0.33	01 ⇌ 99
3	*exo*,*exo*-2,3-Norbornanediol **16**	1.5	01 ⇌ 99
4	1,3-Propanediol **19**	3	15 ⇌ 85

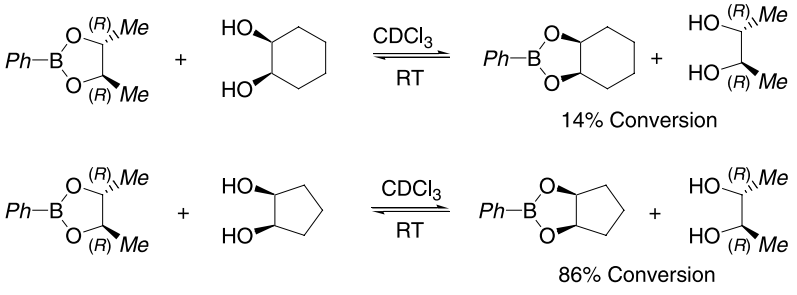

Fig. 8. A comparison of the relative stability of boronic esters **4** and **5**

Table 5. Transesterification of achiral 2-phenyltetrahydrocyclopenta[1,3,2]dioxaborole (**5**) with representative diols in $CDCl_3$

Entry	Diol	Time/h	Equilibrium compositions *RBE* (%) ⇌ *PBE* (%)
1	1,4-Anhydroerythritol **16**	1.0	51 ⇌ 49
2	*cis*-1-Methylcyclopentan-1,2-diol **12**	1.25	37 ⇌ 63
3	*cis*-1-Ethylcyclopentan-1,2-diol **13**	25	27 ⇌ 73
4	*cis*-1-Isopropylcyclopentan-1,2-diol **14**	120	13 ⇌ 87
5	*cis*-1,2-Dimethyl-1,2-cyclopentanediol **15**	720	60 ⇌ 40
6	*exo*,*exo*-2,3-Norbornanediol **17**	48	20 ⇌ 80
7	*endo*-2-Phenyl-*exo*,*exo*-2,3-norbornanediol **18**	264	14 ⇌ 86

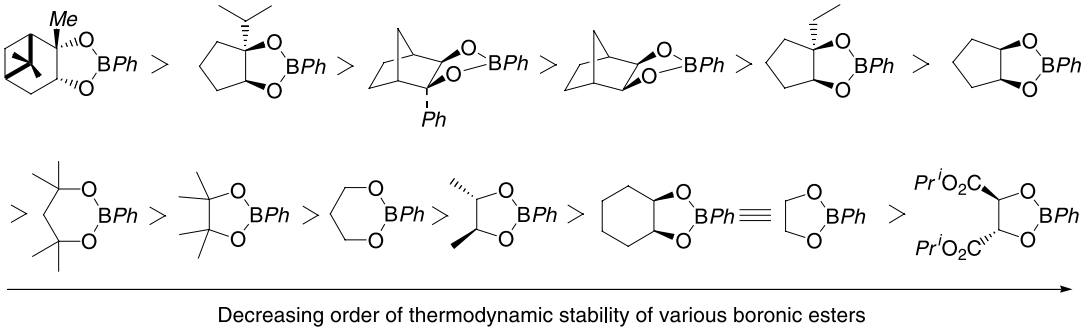

Fig. 9. Order of thermodynamic stability of representative boronic esters

boat-form to attain coplanarity requires an additional energy and therefore makes the process less favorable. A linear relationship between the thermodynamic stability of various substituted cyclopentanediol boronic ester and the steric bulk of the alkyl substituent present at C_1-carbon of *cis*-1,2-cyclopentanediols **12**–**14** (entries 2–4) is well presented in Table 5. The steric bulk of the substituent was anticipated to slow down the exchange process, but expected to produce thermodynamically more stable boronic ester. Indeed, that was the case. It is worth noting that the second substitution at C_2-carbon dramatically slows down the ligand exchange process.

Based on the above experimental data, several representative boronic esters can be arranged in decreasing order of their relative stability (pinanediol boronic ester is most stable and *DIPT* boronic ester is least stable in this series) (Fig. 9).

Conclusions

To summarize, we have studied the relative stability of a wide spectrum of boronic esters (achiral and chiral) employing transesterification with free diols under neutral conditions and compiled them in the decreasing order of their stability. Diisopropyl tartrate (*DIPT*) boronic ester was found to be thermodynamically the least stable boronic ester. Simple six-membered boronic esters were observed to be relatively more stable than their corresponding five-membered analogs. The nature of the substituent present on the carbon bearing the hydroxyl group has greater influence on equilibrium. A coplanar diol favors the formation of the relatively more stable boronic ester. With the knowledge of the relative stability of boronic esters, it is possible to recover the C_2-symmetric chiral auxiliaries, such as, (+)-*DIPT*, (−)-2,3-butanediol, *cis*-1,2-cyclohexanediol, from their boronic esters by transesterification with a series of cheap diols, *e.g.*, ethylene glycol, pinacol, 1,3-propanediol, neopentyl glycol, and diethanolamine. To the best of our knowledge, a general study of this sort had never been done and would be potentially of significant interest to the practicing organic chemist in the boronic acid/ester field.

Experimental

Detailed procedures and techniques for handling air- and moisture-sensitive compounds have been reported elsewhere [35]. The ^{11}B (96 MHz), ^{1}H (300 MHz), and ^{13}C (75 MHz) *NMR* spectra were recorded on a Varian Gemini *NMR* instrument, and the chemical shifts (δ) are given in *ppm* relative to

external standard BF_3-Et_2O and internal standards *TMS* and $CDCl_3$. Except for diols **11**–**14** and **16**–**17**, all the diols were purchased from the Aldrich Chemical Co.

Several boronic esters and diols, such as (−)-4,5-dimethyl-2-phenyl[1,3,2]dioxaborolane (**2**) [36], 4,4,5,5-tetramethyl-2-phenyl[1,3,2]dioxaborolane (**3**) [37], 1-methylcyclopentane-*cis*-1,2-diol (**12**) [37], 1-ethylcyclopentane-*cis*-1,2-diol (**13**) [37], 1-isopropylcyclopentane-*cis*-1,2-diol (**14**) [37], 1,2-dimethylcyclopentane-*cis*-1,2-diol (**15**) [38], bicyclo[2.2.1]-heptane-*exo*,*exo*-2,3-diol (**17**) [39], and 2-phenylbicyclo [2.2.1]heptane-*exo*,*exo*-2,3-diol (**18**) [40], have been well characterized in literature.

*Preparation of Various Boronic Esters **1**–**5***

Following the procedure reported by *Brown et al.* [26], boronic esters **1**–**5** were prepared (5–10 mmol scale) by esterification of phenylboronic acid with the corresponding diols in *n*-pentane (20–30 cm^3) in 4–6 h at room temperature in excellent chemical yield (75–85%) and purity. These boronic esters were characterized by spectroscopic means.

Spectral Data for Various Boronic Esters and Diols

(+)-Diisopropyl (L)-tartrate phenylboronic ester (**1**, $C_{16}H_{21}BO_6$)
^{11}B NMR ($CDCl_3$): $\delta = 26.7$ ppm; ^1H NMR ($CDCl_3$): $\delta =$ 7.35–7.85 (m, 5H, Ar*H*), 5.00 (m, 2H, $-OCH(CH_3)_2$), 4.70 (s, 2H, $-CHOB-$), 1.26 (s, 12H, $-CH_3$) ppm.

(−)-2,3-Butanediol phenylboronic ester (**2**, $C_{10}H_{13}BO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 27.0$ ppm; ^1H NMR ($CDCl_3$): $\delta =$ 7.35–7.85 (m, 5H, Ar*H*), 4.10 (m, 2H, $-OCHCH_3$, 1.35 (d, 6H, $-CHCH_3$) ppm.

4,4,5,5-Tetramethyl-2-phenyl[1,3,2]dioxaborolane (**3**, $C_{12}H_{17}BO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 26.7$ ppm; ^1H NMR ($CDCl_3$): $\delta =$ 7.35–7.85 (m, 5H, Ar*H*), 1.35 (s, 12H, $-CH_3$) ppm.

2-Phenylhexahydrobenzo[1,3,2]dioxaborole (**4**, $C_{12}H_{15}BO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 26.7$ ppm; ^1H NMR ($CDCl_3$): $\delta =$ 7.35–7.85 (m, 5H, Ar*H*), 4.33 (m, 2H, $-CHOB-$), 2.00–1.00 (m, 8H, $-CH_2-$) ppm.

2-Phenyltetrahydrocyclopenta[1,3,2]dioxaborole (**5**, $C_{11}H_{13}BO_2$)
^{11}B NMR ($CDCl_3$): $\delta = 26.7$ ppm; ^1H NMR ($CDCl_3$): $\delta =$ 7.35–7.85 (m, 5H, Ar*H*), 4.80 (m, 2H, $-CHOB-$), 2.20–1.40 (m, 6H, $-CH_2-$) ppm.

1-Methylcyclopentane-cis-1,2-diol (**12**, $C_6H_{12}O_2$)
^1H NMR ($CDCl_3$): $\delta = 3.70$ (1H, m, $-CHOH$), 2.20 (d, 1H, $-CHOH$), 2.06 (s, 1H, $-C(CH_3)OH$), 2.00–1.40 (m, 6H, $-CH_2-$), 1.26 (s, 3H, $-CH_3$) ppm.

1-Ethylcyclopentane-cis-1,2-diol (**13**, $C_7H_{14}O_2$)
^1H NMR ($CDCl_3$): $\delta = 3.95$ (m, 1H, $-CHOH$), 2.45 (br s, 1H, $-CHOH$), 2.30 (br s, 1H, $-C(C_2H_5)OH$), 2.20–1.60 (m, 6H, $-CH_2-$), 1.55 (q, 2H, $-CH_2CH_3$), 0.92 (t, 3H, $-CH_2CH_3$) ppm.

1-Isopropylcyclopentane-cis-1,2-diol (**14**, $C_8H_{16}O_2$)
^1H NMR ($CDCl_3$): $\delta = 3.90$ (m, 1H, $-CHOH$), 2.10 (br s, 2H, $-CHOH$ and $-(CH_3)_2COH$), 2.00–1.40 (m, 7H, $-CH_2-$ and $-CH(CH_3)_2$), 0.95 (dd, 6H, $-CH(CH_3)_2$) ppm.

1,2-Dimethylcyclopentane-cis-1,2-diol (**15**, $C_7H_{14}O_2$)
^1H NMR ($CDCl_3$): $\delta = 2.43$ (s, 2H, $-C(CH_3)OH$), 2.00–1.40 (m, 6H, $-CH_2-$), 1.17 (s, 6H, $-CH_3$) ppm.

Bicyclo[2.2.1]heptane-exo,exo-2,3-diol (**17**, $C_7H_{12}O_2$)
^1H NMR ($CDCl_3$): $\delta = 3.68$ (d, 2H, $-CHOH$), 2.65 (br d, 2H, $-CHOH$), 2.13 (m, 2H, $-CH-$), 1.80–1.00 (m, 6H, $-CH_2-$) ppm.

2-Phenylbicyclo[2.2.1]heptane-exo,exo-2,3-diol (**18**, $C_{13}H_{16}O_2$)
^1H NMR ($CDCl_3$): $\delta = 7.50$–7.20 (m, 5H, Ar*H*), 4.10 (d, 1H, $-CHOH$), 3.10 (d, 1H, $-CHOH$), 2.63 (s, 1H, $-C(Ph)OH$), 2.50–2.10 (m, 3H, $-CH-$), 1.60–1.00 (m, 5H, $-CH_2-$) ppm.

Transesterification Procedure

Transesterification reactions were carried out in NMR tubes under an inert atmosphere. An equimolar mixture of the boronic ester and the diol (0.05 mmol each in 1 cm^3 $CDCl_3$) was taken in $CDCl_3$ (stored over molecular sieves) and sealed with a septum under an inert atmosphere. The ^1H NMR spectra of various exchange reactions were frequently recorded (5–15 min to 12–24 h depending upon the speed of the reaction) to get percentage exchange accurately with time. For slow tranesterifications, the reactions were followed for extended period of time (until no further exchange) even after an equilibrium had reached. The extent of ligand exchange was determined based on the NMR integrations of the relevant proton signals (the error should not exceed $\pm 5\%$ within the NMR detection limit).

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