Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 784–790
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Stability of boronic esters – Structural effects on the relative rates of transesterification of 2-(phenyl)-1,3,2-dioxaborolane ☆

Chandra D. Roy *, Herbert C. Brown

Department of Chemistry, H.C. Brown Center for Borane Research, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084, USA

Received 9 July 2006; received in revised form 7 October 2006; accepted 7 October 2006
Available online 14 October 2006

This paper is dedicated to the memory of my mentor, the late Professor Herbert C. Brown (1912–2004).

Abstract

Relative rates of reaction of the achiral cyclic phenylboronic ester 2-(phenyl)-1,3,2-dioxaborolane with a wide variety of structurally modified diols, have been studied to understand the factors influencing the relative stabilities of boronic esters. It is found that the alkyl substituents on the α-carbons of diols slow down the transesterification, but produce thermodynamically more stable boronic ester. Six-membered boronic esters are thermodynamically more stable than their corresponding five-membered analogs. Amongst cyclic 1,2-diols, *cis*-1,2-cyclopentanediol displaces ethylene glycol instantaneously whereas *trans*-1,2-cyclopentanediol is totally unreactive, which suggests that the *cis*-stereochemistry of the 1,2-diol is a prerequisite for transesterification. Among the 1,5-diols, diethanolamine displaces ethylene glycol quite rapidly forming a more stable bicyclic chelate in which nitrogen is attached to boron by a coordinating bond (as evident by ^{11}B NMR spectroscopy). The oxygen atom of di(ethylene glycol) and the sulfur atom of 2,2′-thiodiethanol do not assist in displacing the ethylene glycol from their boronic esters.

Keywords: Boronic esters; Diols; Transesterification; Stability; Chiral auxiliaries

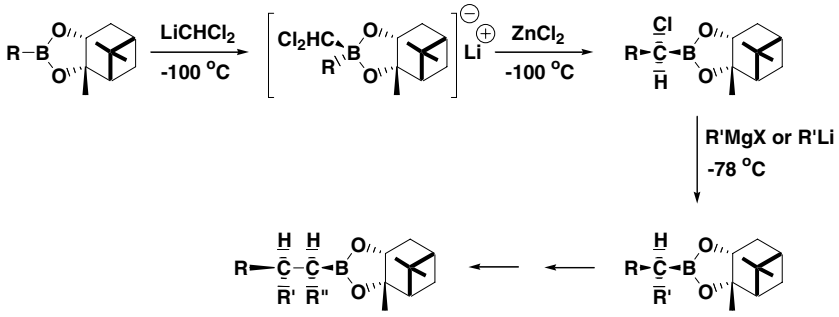
1. Introduction

Boronic acids and their esters are highly valuable compounds which have found extensive applications in organic and medicinal chemistry [1a,1b,1c,1d,1e,1f]. Some of their uses include, protecting groups in carbohydrate chemistry, [1g] general substrates in the Suzuki coupling [1h] and the Petasis reactions, [1i] chiral derivatizing agents, [1j,1k] redox-sensitive protecting group [1l] and glucose-selective fluorescence sensor [1m]. Asymmetric synthesis has proven to be a very effective method for the preparation of enantiomerically pure compounds of chemical and biological relevances. The discovery of asymmetric hydroboration in 1961 using diisopinocampheylborane (Ipc_2BH) marked the beginning of an effective asymmetric synthesis [2,3]. Since then, tremendous interest has developed to make the asymmetric synthesis methodically rich and efficient. Matteson and co-workers [4] achieved a very high degree of stereo- and enantio-selectivities (>99% ee) during the successive one-carbon homologation of cyclic boronic esters derived from pinanediol with preformed (dichloromethyl)lithium (Scheme 1). This elegant successive asymmetric homologation not only predicts the chirality at each chiral center, but also introduces additional chiral centers without limit. But due to the unusual resistance of pinanediol boronic esters toward hydrolysis, transesterification or ligand exchange, remarkable difficulties were experienced in recovering the costly chiral auxiliary, pinanediol. In 1988, we developed convenient procedures for the recovery

☆ The work described herein was performed at Purdue University (1997–2001). Preliminary results were presented at the *H.C. Brown Lectures in Organic Chemistry*, Purdue University, April 4,1998.

* Corresponding author. Present address: EMD Biosciences, Inc., 10394 Pacific Center Court, San Diego, CA 92121, USA. Tel.: +1 858 450 5618; fax: +1 858 453 3552.
E-mail address: chandra61804@yahoo.com (C.D. Roy).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.10.013



Scheme 1. Matteson's asymmetric homologation.

of pinanediol from pinanediol boronic esters [5]. Recently, Hutton et al. [6] reported a mild alternate method for the deprotection of pinacol boronic ester utilizing polystyrene-boronic acid (competing boronic acid instead of a diol) via transesterification.

Boronic esters have proven to be of great importance in asymmetric synthesis [7]. The easy introduction and recovery of chiral auxiliaries is the key factor in a chiral auxiliary directed multistep stereo- and enantio-selective synthesis. Transesterification is the one of the simplest, convenient, gentle procedures which can introduce and also recover the chiral auxiliaries to or from boronic esters, provided the former boronic ester is thermodynamically less stable than the latter. This persuaded us to undertake a systematic study of the relative rates of transesterification of five-membered boronic ester, 2-(phenyl)-1,3,2-dioxaborolane with various structurally modified diols to understand the factors influencing the stabilities of boronic esters and the results of such study are described in this publication.

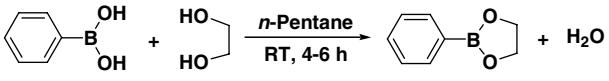
2. Results and discussion

2.1. Preparation of 2-(phenyl)-1,3,2-dioxaborolane

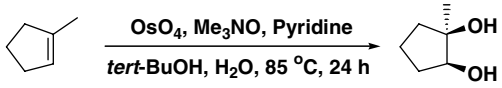
2-(Phenyl)-1,3,2-dioxaborolane was prepared in excellent yield by treating phenylboronic acid (5.0 mmol) with ethylene glycol (5.0 mmol) in *n*-pentane (15 mL) for 4–6 h at room temperature. The product was characterized by spectroscopic means (Scheme 2) [8–10].

2.2. Preparation of 1-methyl-cis-1,2-cyclopentanediol

Following the procedure reported by Ray and Matteson [11], substituted *cis*-1,2-cyclopentanediols, *cis*-acenaphthylenediol and *exo,exo*-2,3-norbornanediol were prepared in excellent chemical yields (>90%) by OsO_4-catalysed *cis*-dihydroxylation of the corresponding olefins and were subsequently characterized by ^1H and ^{13}C NMR spectroscopy (Scheme 3).



Scheme 2. Reaction of phenylboronic acid with ethylene glycol in *n*-pentane.



Scheme 3. Dihydroxylation of 1-methylcyclopentene with OsO_4.

2.3. Types of diols examined

In order to compare the electronic and steric effects on transesterification of boronic ester with various diols, we examined a wide variety of acyclic and cyclic diols which are categorized below (Chart 1). Transesterifications (0.05 mmol scale) were carried out in $CDCl_3$ solvent in NMR tubes under inert atmosphere and the progress of the reactions were monitored by ^1H NMR spectroscopy.

2.4. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative acyclic 1,2-diols: substituent effects

Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with 1,2-propanediol **1** gives an equilibrium mixture favoring 1,2-propanediol phenylboronic ester (68.6%) in less than 0.1 h, which suggests that monosubstituted ethylene glycol boronic ester is thermodynamically more stable than its unsubstituted analog (Scheme 4, Table 1). Introduction of a second methyl substituent further increases the thermodynamic stability of the boronic ester, as evident from the equilibrium composition obtained in the case of *meso*-2,3-butanediol **2** (74.7%). Pinacol **3**, being a sterically hindered diol, displaces ethylene glycol very slowly, but produces a thermodynamically more stable boronic ester than those of 1,2-propanediol and *meso*-2,3-butanediol, shifting the equilibrium towards the pinacolboronic ester (87.8%). (+)-Diisopropyl tartrate (DIPT) **4** gave no appreciable amounts of DIPT boronic ester (<5%) suggesting that the DIPT boronic ester is thermodynamically the least stable boronic ester in this series. To test this unfavorable equilibrium with DIPT, DIPT phenylboronic ester was prepared and subjected to transesterification with ethylene glycol under identical conditions. There was an instantaneous quantitative displacement of DIPT from its boronic ester

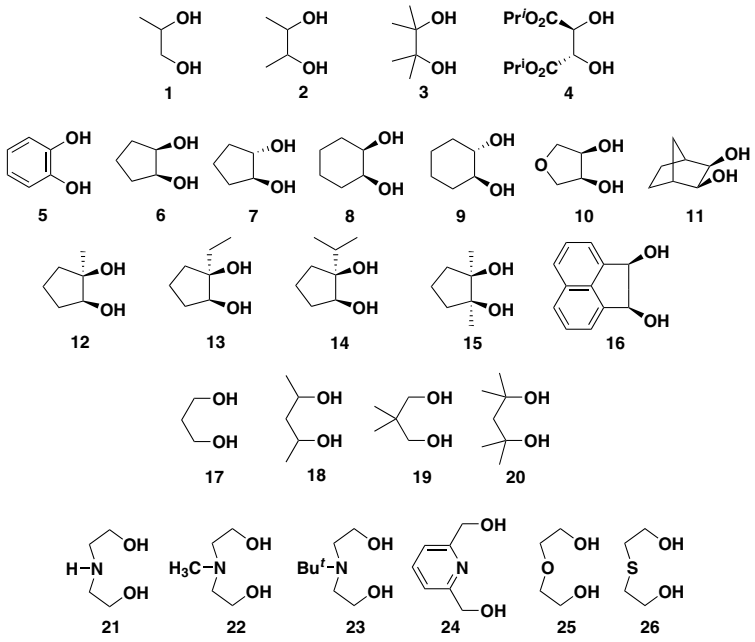


Chart 1. Diols of diverse structural types.

by ethylene glycol which confirms our conclusion. This observation clearly indicates that the chiral auxiliary diisopropyl tartrate can be very easily retrieved and recycled from its boronic ester with a very cheap diol like ethylene glycol or pinacol. The reaction profiles are depicted in Fig. 1.

2.5. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with cyclic 1,2-diols: ring strain and conformational effects

Next we became interested in examining cyclic 1,2-diols, **5**–**11** which might differ in reactivity due to both ring strain and conformational factors. The experimental results are presented in Table 2 and the reaction profiles in Fig. 2. The poor reactivity of catechol **5** during transesterification may be attributed to the lower nucleophilicity of the hydroxyl oxygen due to the presence of the phenyl ring. In the case of *cis*-1,2-cyclopentanediol **6**, the exchange is over instantaneously (<5 min), forming the more stable *cis*-1,2-cyclopentanediol phenylboronic ester in >99% chemical yield, whereas *trans*-1,2-cyclopentanediol **7** showed no appreciable transesterification even after 47 h. In order to compare the effect of ring strain on rates and

Scheme 4. General scheme for transesterification of 2-(phenyl)-1,3,2-dioxaborolane with various diols **1**–**4**.

Table 1
Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative substituted 1,2-ethanediols **1**–**4** at ambient temperature

Entry	1,2-Diol	Time (h)	% Transesterification
1	1,2-Propanediol **1**	0.1	68.6
2	*meso*-2,3-Butanediol **2**	0.1	74.7
3	Pinacol **3**	94	87.8
4	(+)-Diisopropyl Tartrate **4**	0.1	4.5

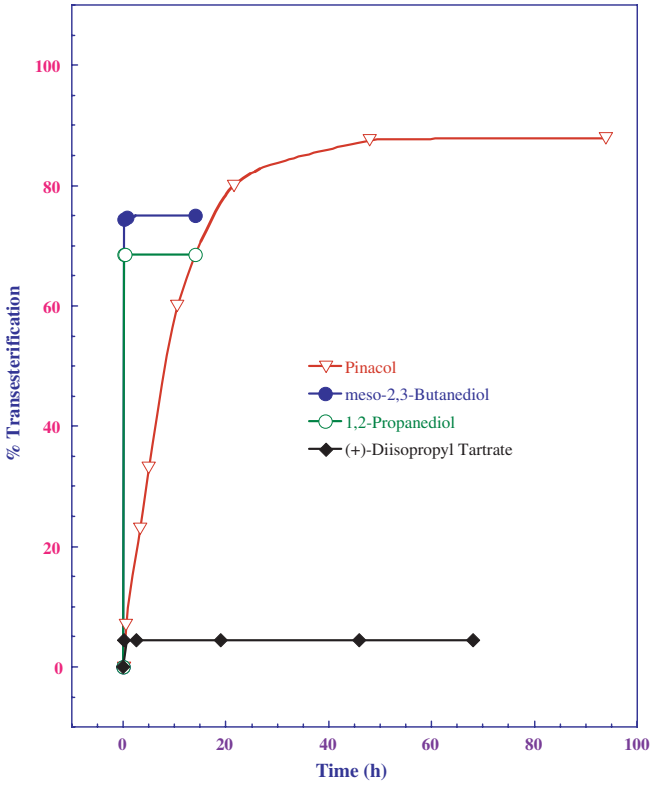


Fig. 1. Transesterification of ethylene glycol phenylboronic ester (0.05 M) with various 1,2-diols **1**–**4** (0.05 M) in $CDCl_3$ at 25 °C.

Table 2
Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with cyclic 1,2-diols **5**–**11** at ambient temperature

Entry	1,2-Diol	Time (h)	% Transesterification
1	Catechol **5**	5	28
2	*cis*-1,2-Cyclopentanediol **6**	0.1	99
3	*trans*-1,2-Cyclopentanediol **7**	47	0
4	*cis*-1,2-Cyclohexanediol **8**	0.1	47
5	*trans*-1,2-Cyclohexanediol **9**	44	0
6	1,4-Anhydroerythritol **10**	0.75	97
7	*exo,exo*--2,3-Norbornanediol **11**	0.1	99.5

equilibria, we carried out the transesterification with both *cis*- and *trans*-1,2-cyclohexanediols.

cis-1,2-Cyclohexanediol **8** produces an equilibrium mixture favoring *cis*-1,2-cyclohexanediol phenylboronic ester by only 47% which suggests that the starting ethylene glycol phenylboronic ester is slightly more stable than the product. Like *trans*-1,2-cyclopentanediol, *trans*-1,2-cyclohexanediol **9** was also found to be an inert. The replacement of a CH_2 group with an oxygen heteroatom slightly decreases the product ratio (1,4-anhydroerythritol **10** showed only 97% transesterification). *exo,exo*-2,3-Norbornanediol **11**, being a 3,5-disubstituted 1,2-cyclopentanediol, displays similar reactivity as observed in the case of *cis*-1,2-cyclopentanediol. These results unambiguously suggest that both ring strain and the stereochemistry of the reacting diol influence the rates and equilibria during transesterification. The *cis*-stereochemistry of the diol is a prerequisite for an intramolecular transesterification. The ring strain on the diol accelerates the reaction rate and also favors the equilibrium towards thermodynamically more stable cyclic boronic ester. This study also reveals that stereoisomeric diols, such as cyclic *cis*- and *trans*-1,2-diols could be very easily resolved using transesterification methodology.

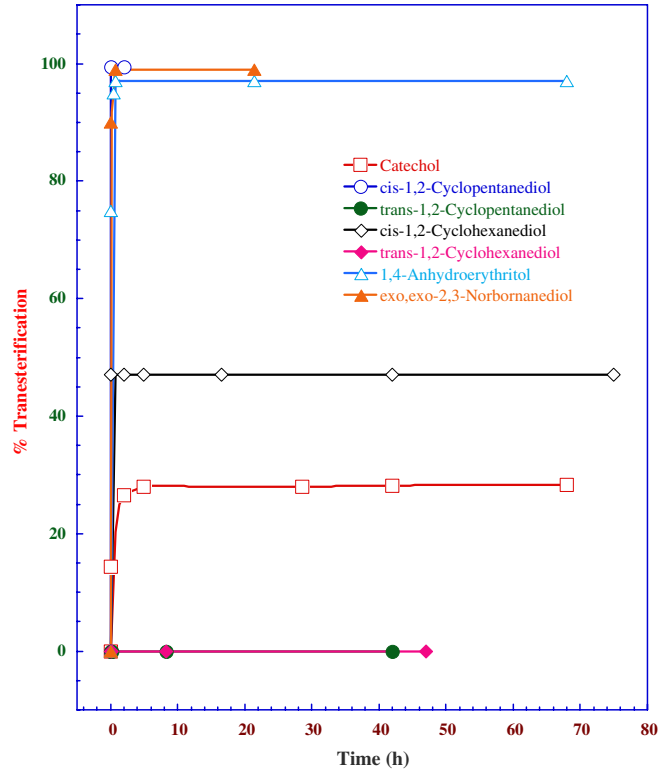


Fig. 2. Transesterification of ethylene glycol phenylboronic ester (0.05 M) with various 1,2-diols **5**–**11** (0.05 M) in $CDCl_3$ at 25 °C.

2.6. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative cis-1,2-cyclopentanediols: substituent effects

Encouraged by the results obtained from *cis*-1,2-cyclopentanediols **12**–**16**, we decided to examine the steric effects on the rates and equilibria of boronic esters during transesterification. It is quite clear from the experimental results that an introduction of alkyl group on the diol certainly slows down the reaction rate, but yields thermodynamically more stable substituted cyclopentanediol boronic esters (Table 3). *cis*-1,2-Dimethyl-1,2-cyclopentanediol **15** appears to be most hindered diol in the cyclopentanediol series. In order to test the thermodynamic stability of *cis*-1,2-dimethyl-1,2-cyclopentanediol boronic ester, it was treated with (+)-α-pinanediol.

α-Pinanediol which normally displaces cyclopentanediols and other diols relatively rapidly from boronic esters, could displace only 5–6% of *cis*-1,2-dimethyl-1,2-cyclopentanediol after 15 days which proves that *cis*-1,2-dimethyl-1,2-cyclopentanediol boronic ester is thermodynamically most stable in the cyclopentanediol series. The relative slowness of the reaction is directly related to the substituent bulk on the diol. It is hoped that *cis*-1,2-acenaphthylenediol **16**, being a rigid system, might show improved results, but only comparable results were obtained. These results are represented graphically in Fig. 3.

2.7. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with acyclic 1,3-diols: ring size and substituent effects

The correlation between the relative stability of a cyclic compound and the ring size is well studied and understood. In order to compare the stabilities of five-membered boronic esters with six-membered boronic esters, we

Table 3
Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative substituted *cis*-1,2-cyclopentanediols **12**–**16** at ambient temperature

Entry	1,2-Diol	Time (h)	% Transesterification
1	*cis*-1-Methyl-1, 2-cyclopentanediol **12**	0.75	99
2	*cis*-1-Ethyl-1, 2-cyclopentanediol **13**	1.5	99
3	*cis*-1-Isopropyl-1,2-cyclopentanediol **14**	1.75	99
4	*cis*-1,2-Dimethyl-1,2-cyclopentanediol **15**	258	99
5	*cis*-1,2-Acenaphthylenediol **16**	2.5	97

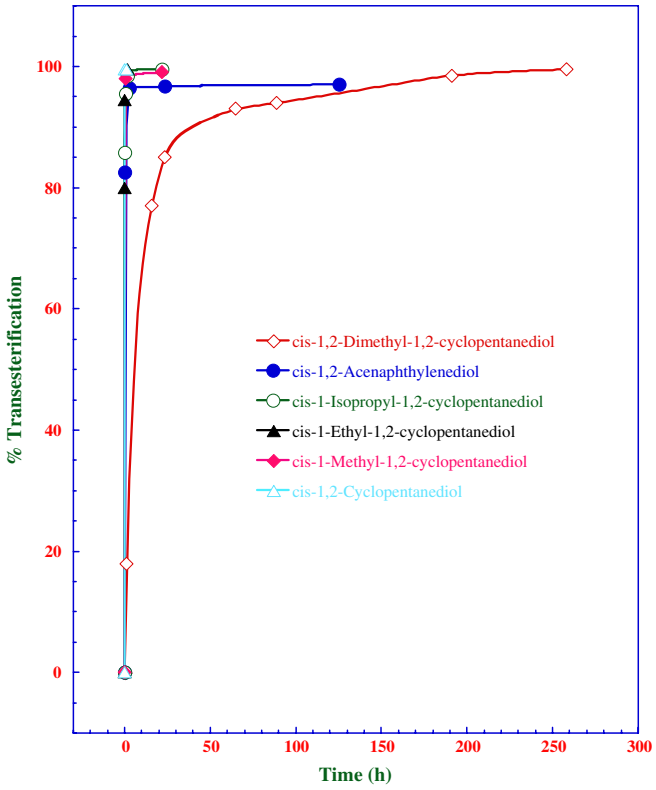


Fig. 3. Transesterification of ethylene glycol phenylboronic ester (0.05 M) with various 1,2-diols **12**–**16** (0.05 M) in $CDCl_3$ at 25 °C.

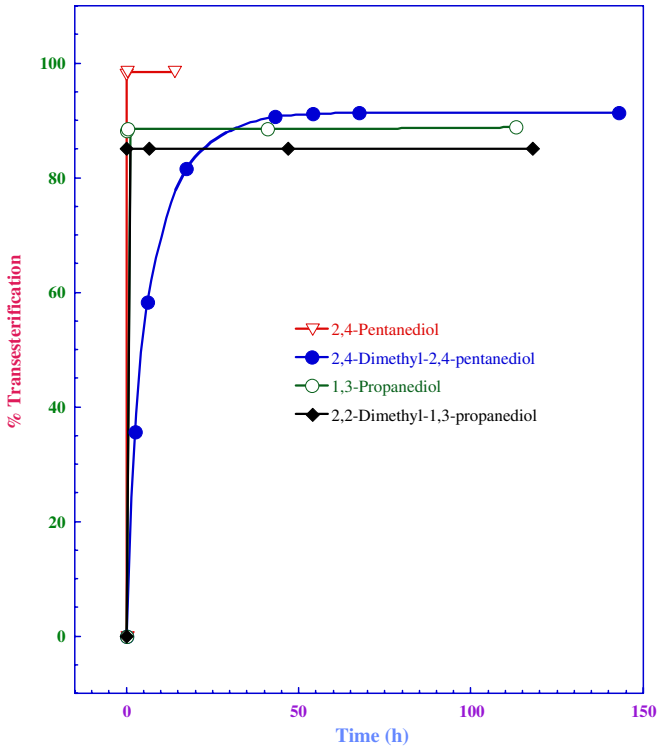


Fig. 4. Transesterification of ethylene glycol phenylboronic ester (0.05 M) with various 1,2-diols **17**–**20** (0.05 M) in $CDCl_3$ at 25 °C.

decided to examine the relative rates of 2-(phenyl)-1,3,2-dioxaborolane with four representative 1,3-diols **17**–**20**.

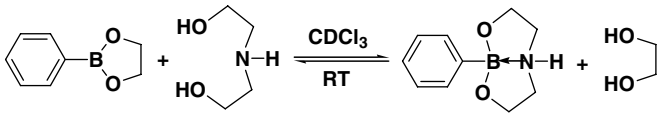
1,3-Propanediol **17** gives an equilibrium mixture which has 88.5% six-membered boronic ester. This clearly suggests that six-membered boronic ester is thermodynamically more stable than five-membered boronic ester. In order to examine the steric effects on rates and equilibria during transesterification, three substituted 1,3-diols are treated with 2-(phenyl)-1,3,2-dioxaborolane under identical conditions. It is clear from Table 4 that an introduction of two methyl groups at 1,3-position shifts the equilibrium (from 88.5% to 98%) towards more stable 2,4-pentanediol phenylboronic ester. Further substitution at C-2 and C-4 positions of 2,4-pentanediol, e.g., 2,4-dimethyl-2,4-pentanediol **20** not only slows down the exchange process, but also produces boronic ester of lower stability (as reflected by the equilibrium composition) in comparison with 2,4-pentanediol **18**. The substitution of methyl groups at C-2 position has no significant effects on the equilibrium composition as seen with neopentyl glycol **19**. These results are represented graphically in Fig. 4.

Table 4
Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative 1,3-diols 17–20 at ambient temperature

Entry	1,2-Diol	Time (h)	Transesterification (%)
1	1,3-Propanediol **17**	0.1	88.5
2	2,4-Pentanediol **18**	0.1	98
3	2,2-Dimethyl-1, 3-propanediol **19**	0.1	85
4	2,4-Dimethyl-2, 4-pentanediol **20**	67	91

2.8. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative 1,5-diols: Effects of chelation by heteroatoms

It is well known that diethanolamine forms stable chelated complexes with boronic acids. Persuaded by this fact, we studied the rates and equilibria of few amino-1,5-diols **21**–**26** with boronic ester (Scheme 5). Diethanolamine **21** undergoes transesterification quantitatively in <5 min as seen by ^{11}B and ^{1}H NMR spectroscopy (Table 5). Jung et al. [12] and Iovine et al. [13] have independently utilized diethanolamine/HCl to deprotect pinacol from their boronic esters to get free boronic acids. *N*-methyldiethanolamine **22** was observed to be slightly less effective (70% displacement) than the diethanolamine. Surprisingly, *N*-*tert*-butyldiethanolamine **23**, which was hoped to show more effective chelation due to increased basicity of the nitrogen due to the presence of the highly electron releasing



Scheme 5. Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with 1,5-diols **21**–**26**.

Table 5
Transesterification of 2-(phenyl)-1,3,2-dioxaborolane with representative 1,5-diols **21**–**26** at ambient temperature

Entry	1,2-Diol	Time (h)	Transesterification (%)
1	Diethanolamine **21**	0.1	99
2	*N*-methyldiethanolamine **22**	0.5	70
3	*N*-*tert*-butyldiethanolamine **23**	72	0
4	2,6-Pyridinedimethanol **24**	129	9
5	Di(ethylene glycol) **25**	70	0
6	2,2′-Thiodiethanol **26**	69	0

tert-butyl group, did not furnish any appreciable amount of chelated boronic ester. Earlier, *N*-methyldiethanolamine and the sodium salt of bicine were tested in the recovery of pinanediol from pinanediol boronic esters, but without any success. 2,6-Pyridinedimethanol **24** shows only small amount of chelated boronic ester (<10%).

The oxygen and the sulphur atoms of diethyl ether (EE), tetrahydrofuran (THF) and dimethylsulfide (DMS) are known to coordinate with boron atoms to form stable adducts. The strength of these coordinated X–B bonds depends upon the nature of the substituents present on both species. Therefore, it was interesting to examine how the oxygen atom of di(ethylene glycol) **25** and the sulphur atom of 2,2′-thiodiethanol **26** coordinate with the boron atom of the boronic ester, 2-(phenyl)-1,3,2-dioxaborolane, and facilitate the transesterification. Unfortunately, neither coordination between oxygen and boron or sulphur and boron atoms nor any chelated boronic ester formation is observed (as seen by ^{11}B and ^{1}H NMR spectroscopy). These results are depicted in Fig. 5.

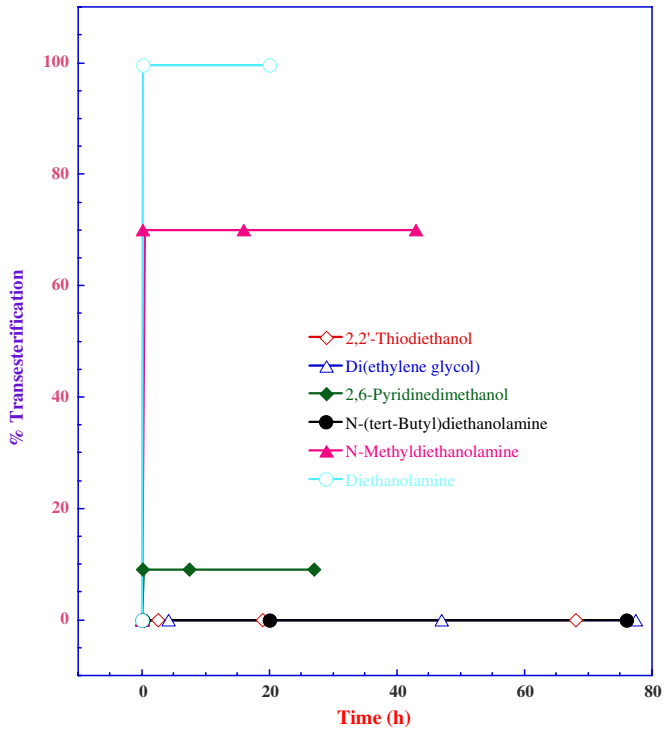


Fig. 5. Transesterification of ethylene glycol phenylboronic ester (0.05 M) with various 3-heteroatom substituted 1,5-diols **21**–**26** (0.05 M) in $CDCl_3$ at 25 °C.

3. Conclusions

Relative rates and equilibrium compositions resulting from the reactions of an achiral cyclic phenylboronic ester, 2-(phenyl)-1,3,2-dioxaborolane, with a wide variety of diols of varied structural types, have been examined to understand the factors influencing the relative stabilities of boronic esters. Experimental results have shown that the alkyl substituents on α-carbons of diols slow down the transesterification, but produce the thermodynamically more stable boronic ester. Six-membered boronic esters have been observed to be thermodynamically more stable than their corresponding five-membered analogs. Amongst cyclic 1,2-diols, *cis*-1,2-cyclopentanediol displaced ethylene glycol instantaneously whereas *trans*-1,2-cyclopentanediol was found to be totally inert. Interestingly, *cis*-1,2-cyclohexanediol could displace ethylene glycol only up to 48% (again, the *trans*-isomer was found to be inactive), which indicates that the higher reactivity of *cis*-1,2-cyclopentanediol may be due to ring strain. A systematic study of the steric effects of alkyl substituents on *cis*-1,2-cyclopentanediols during transesterification revealed that the isopropyl group was the best substituent among the alkyl groups studied in driving the equilibrium towards right-hand side, yielding thermodynamically more stable boronic ester. *cis*-1,2-Dimethyl-1,2-cyclopentanediol has been found to be the most sterically hindered diol in the cyclopentanediol series. Among the 1,5-diols, diethanolamine displaces ethylene glycol quite rapidly forming a more stable bicyclic chelate in which nitrogen is linked to boron by a coordinating bond (as evidenced by ^{11}B NMR spectroscopy). *N*-Methyldiethanolamine was comparatively a less effective (70%) chelating agent than the diethanolamine (99%) in the case of ethylene glycol phenylboronic ester. Surprisingly, *N*-*tert*-butyldiethanolamine failed to displace ethylene glycol, suggesting that such an equilibrium was unfavorable due to the presence of the *tert*-butyl group on nitrogen. The oxygen atom of di(ethylene glycol) and the sulfur atom of 2,2′-thiodiethanol also did not facilitate the displacement of ethylene glycol from its boronic ester. In conclusion, this study not only provided useful insights about the factors influencing the thermodynamic stability of various boronic esters, but also led us to resolve structural and stereoisomeric diols in a very practical and efficient way which will be reported in due course. Also, many expensive C_2-symmetric chiral diol auxiliaries, such as (+)-2,3-butanediol, (+)-2,4-propanediol and (−)-diisopropyl tartrate (DIPT), can be retrieved from the boronic esters using cheap diols.

4. Experimental

4.1. General

All of the diols were commercially available (Aldrich) except *exo,exo*-2,3-norbornanediol **11**, *cis*-1-methyl-1,2-cyclopentanediol **12**, *cis*-1-ethyl-1,2-cyclopentanediol **13**, *cis*-1-isopropyl-1,2-cyclopentanediol **14**, *cis*-1,2-dimethyl-1,2-cyclopentanediol **15** and *cis*-1,2-acenaphthylenediol **16**, which were prepared by OsO_4-catalysed *cis*-dihydroxylation of their corresponding olefins. The starting material, 2-(phenyl)-1,3,2-dioxaborolane was prepared in excellent yield by esterifying phenylboronic acid (5.0 mmol) with ethylene glycol (5.0 mmol) in *n*-pentane (15 mL) for 4–6 h at room temperature. Water formed during the reaction can very easily be removed by adding molcular sieves or drying agents (anhydrous Na_2SO_4 or $MgSO_4$). The product was characterized by spectroscopic means (^{11}B and ^1H NMR, Varian-Gemini, 300 MHz). All transesterification reactions were carried out in $CDCl_3$ solutions (0.05 mmol) of both boronic ester and the desired diol in 1.0 mL $CDCl_3$ in NMR tubes under an inert atmosphere. The progress of the reactions was followed by ^1H NMR spectroscopy.

Acknowledgements

Financial support from the Purdue Borane Research Fund is gratefully acknowledged. We also thank Professor Donald S. Matteson for his interest and encouragement.

References

[1] (a) D.G. Hall (Ed.), Boronic Acids: Preparations and Applications in Organic Synthesis and Medicine, Wiley–VCH, Weinheim, 2005;
(b) D.S. Matteson, Tetrahedron 45 (1989) 1859;
(c) D.S. Matteson, Chemtech 29 (1999) 6;
(d) D.S. Matteson, J. Organomet. Chem. 581 (1999) 51;
(e) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633;
(f) W. Wang, X. Gao, B. Wang, Med. Res. Rev. 23 (2003) 346, and references cited therein;
(g) T.D. James, S. Sandanayake, S. Shinkai, Angew. Chem., Int. Ed. Engl. 35 (1996) 1911;
(h) R. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(i) N.A. Petasis, Z.D. Patel, Tetrahedron Lett. 41 (2000) 9607;
(j) K. Burgess, A.M. Porte, Angew. Chem., Int. Ed. Engl. 33 (1994) 1182;
(k) S. Morandi, E. Caselli, A. Forni, M. Bucciarelli, G. Torre, F. Prati, Tetrahedron: Asymmetr. 16 (2005) 2918;
(l) J. Yan, S. Jin, B. Wang, Tetrahedron Lett. 46 (2005) 8503;
(m) V.V. Karnati, X. Gao, S. Gao, W. Wang, S. Ni, S. Sankar, B. Wang, Bioorg. Med. Chem. Lett. 12 (2002) 3373.
[2] J.D. Morrison (Ed.), Asymmetric Synthesis, vols. 1–5, Academic Press, New York, 1983.
[3] H.C. Brown, G. Zweifel, J. Am. Chem. Soc. 83 (1961) 486.
[4] (a) D.S. Matteson, Stereodirected Synthesis with Organoboranes, Springer, Berlin, 1995, Chapter. 5;
(b) D.S. Matteson, K.M. Sadhu, M.L. Peterson, J. Am. Chem. Soc. 108 (1986) 810;
(c) L. Carmes, F. Carreaux, B. Carboni, J. Org. Chem. 65 (2000) 5403;
(d) D.S. Matteson, H.W. Man, O.C. Ho, J. Am. Chem. Soc. 118 (1996) 4560;
(e) H.C. Brown, P.V. Ramachandran, Pure Appl. Chem. 66 (1994) 201;
(f) D.S. Matteson, Pure Appl. Chem. 63 (1991) 339;
(g) D.S. Matteson, Chem. Rev. 89 (1989) 1535;
(h) M.M. Midland, J. Org. Chem. 63 (1998) 914.
[5] H.C. Brown, M.V. Rangaishenvi, J. Organomet. Chem. 358 (1988) 15.
[6] T.E. Pennington, C. Kardiman, C.A. Hutton, Tetrahedron Lett. 45 (2004) 6657.
[7] D.S. Matteson, Acc. Chem. Res. 21 (1988) 294.
[8] H.C. Brown, N.G. Bhat, V. Somayaji, Organometallics 2 (1983) 1311.
[9] H.C. Brown, T.E. Cole, Organometallics 2 (1983) 1316.
[10] (a) H.C. Brown, S.M. Singh, Organometallics 5 (1986) 994;
(b) P.R. Blakemore, S.P. Marsden, H.D. Vater, Organic Lett. 8 (2006) 773;
(c) H.C. Brown, A.S. Phadke, Synlett (1993) 927.
[11] R. Ray, D.S. Matteson, Tetrahedron Lett. 21 (1980) 449.
[12] M.E. Jung, T.I. Lazarova, J. Org. Chem. 64 (1999) 2976.
[13] E.K. Perttu, M. Arnold, P.M. Iovine, Tetrahedron Lett. 46 (2005) 8753.