RESEARCH FRONT

CSIRO PUBLISHING

Aust. J. Chem. **2011**, *64*, 1415–1416
http://dx.doi.org/10.1071/CH11394

Foreword

Boron Chemistry in the Pacific

Todd A. Houston

Institute for Glycomics, Gold Coast Campus, Griffith University, Qld 4222, Australia.
Email: t.houston@griffith.edu.au

It is fitting that a number of boron chemists convened in Hawaii amid the Pacific Ocean for a special Boronic Acids Symposium at PacifiChem in December 2010. Boron is after all one of the 10 most abundant elements in seawater.[1] In addition, 2010 was a year when an organoboron pioneer, Professor Akira Suzuki, was awarded the Nobel Prize in Chemistry for the palladium-catalyzed coupling of boronic acids that now bears his name.[2] In fact, some of the participants at PacifiChem 2010 came directly from the Nobel Prize Ceremonies in Stockholm held during the week preceding the conference. This special issue of the *Australian Journal of Chemistry* highlights several of the research developments presented at PacifiChem 2010. This is the second special issue of *AJC* dedicated to organoboron pursuits, the first appearing in November 2007.[3]

The Boronic Acids Symposium at PacifiChem dealt with a variety of topics from carbohydrate sensing to bioactive boron compounds to boronates' use in synthesis and catalysis. Two communications from the Taylor and Strongin groups represent important developments in the field of carbohydrate sensors. Taylor describes the use of diarylborinic acids for diol and hydroxyacid receptors.[4] Fluorescent sensing of carbohydrates by boronic acids is a relatively young field less than two decades old[5] and targeting α-hydroxycarboxylates specifically with fluorescent boronates has only developed in the past decade.[6] However, little attention has been paid to borinic acids in these contexts. Taylor and co-workers have shown that borinic acids are particularly effective at binding to catechol-type systems.[4] Relative to analogous arylboronic acids, diarylborinic acids offer an additional handle for synthetic modification to tune the affinity and selectivity of boron-based receptors. Each aromatic group can be introduced sequentially offering an expanded number of potential analogues that can be accessed. Strongin reports success of a diboronate receptor for monitoring clinical adenylosuccinate lyase (ADSL) deficiency by detecting the metabolite 5-aminoimidazole-4-carboxamide riboside (AICAr) in urine.[7] This method uses multidimensional fluorescence measurements recently developed for their diboronate receptor of AICAr.[8] Other methods available for its detection are more time-intensive and some lead to a high rate of false positives.

In related work important in the clinical sensing arena, Skene and co-workers have defined a method for predicting which amine-based boronate fluorophores might be useful under physiological conditions.[9] By studying the fluorescence of amine fluorophores in the presence of phenylboronic acid, the suitability of conjugated aminoboronate compounds as saccharide sensors can be empirically predicted. This should allow for more rapid selection of which aminoboronates should be synthesized as sugar sensors, eliminating the need to make large numbers of compounds up front. In a complementary approach, our own group presents work assessing the feasibility of self-assembled boronate receptors[10] for sensing free sialic acid in comparison to previous covalently linked diboronates.[11] Elevated levels of this monosaccharide can indicate the presence of cancer or other health problems. During the course of this study it was discovered the simple compound *m*-aminophenylboronic acid has appreciable affinity for sialic acid (Neu5Ac).[10]

The bioactivity of organoboron compounds has been studied by Duggan, in the context of their anti-termite properties, and Nakamura, whose group is pursuing carborane derivatives as topoisomerase inhibitors. The Duggan group synthesized a series of spiroborates of α-hydroxycarboxylates and of oxalate and showed that each of these was more toxic to termites than boric acid alone and each offered comparable levels of termite protection in treated paper/wood.[12] Nakamura describes the development of carborane-triazines as topoisomerase inhibitors.[13] Compounds displaying selective and potent inhibition of both topoisomerase I and II were identified.

Several research groups have published advances in synthetic chemistry through use of boronic acid derivatives. Yamamoto and co-workers describe successful asymmetric addition of arylboronates to imines as a method for the synthesis of α-aminoacids.[14]

Todd A. Houston hails from Lamoni, Iowa, USA, and completed a Chemistry B.S. (cum laude) in his hometown at Graceland College in 1987. He earned a Ph.D. from the University of Michigan, Ann Arbor, in 1993 for work on the synthesis of steroidal glycosides with Professor Masato Koreeda. Following an NIH post-doctoral fellowship at Johns Hopkins with Professor Craig Townsend he began his independent career at Virginia Commonwealth University in 1996. In 2001, he moved to Griffith University where he is currently Senior Lecturer in the School of Biomolecular and Physical Sciences and Research Leader at the Institute for Glycomics. In addition to work on boron–carbohydrate interactions described in this issue, he is interested in carbohydrate-based drugs (such as aminoglycosides and glycosidase inhibitors) for tuberculosis, leishmaniasis, and other diseases.

These Rh-catalyzed reactions give consistently high ees (>95 %) for furan-containing products where this heterocycle was used as a masked carboxylic acid synthon. Matteson, a pioneer in the α–functionalization of alkylboronates, describes the synthesis of a simple but useful compound (hydroxymethyl)boronic acid and its pinenediol ester.[15] Extensive stability studies conducted as part of this work should prove instructive to chemists using these species in synthesis. Ishihara and co-workers have recently communicated the development of a bifunctional boronic acid catalyst for the synthesis of cyclic anhydrides and imides from diacids.[16] In further work described in this issue, the authors have dissected the precise structural components that are required for an active catalyst.[17] Boron acids are effective dehydrative catalysts for other transformations of diacids such as monoesterification.[3e] Finally, Churches provides a short Focus Paper on *N*-methyliminodiacetate (MIDA) boronate esters.[18] These have been developed by Burke and co-workers to render boronic acids inert to conditions where they would normally react while still serving as effective substrates for Suzuki-Miyaura couplings.[19]

This special issue highlights but a small portion of the boronic acid chemistry presented at PacifiChem in 2010. Over 40 scientists from both academia and industry gave oral and poster presentations at the Boronic Acid Symposium. Thank you to Binghe Wang, Dennis Hall, Peter Duggan and Michinore Suginome for organizing an excellent week. Based on the expansion of this symposium from the inaugural event at the PacifiChem 2005 conference, we can anticipate an even larger event in 2015. We hope to see many of you there!

References

[1] R. C. Weast, Ed., *CRC Handbook for Chemistry and Physics* **1984**, 65th Edition, CRC Press: Florida.

[2] A. Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722. doi:10.1002/ANIE.201101379

[3] (a) N. A. Petasis, *Aust. J. Chem.* **2007**, *60*, 795. doi:10.1071/CH07360
(b) P. F. Kaiser, Q. I. Churches, C. A. Hutton, *Aust. J. Chem.* **2007**, *60*, 799. doi:10.1071/CH07103
(c) T. A. Houston, S. M. Levonis, M. J. Kiefel, *Aust. J. Chem.* **2007**, *60*, 811. doi:10.1071/CH07222
(d) J. A. Ioppolo, C. J. Kepert, D. J. Price, L. M. Rendina, *Aust. J. Chem.* **2007**, *60*, 816. doi:10.1071/CH07232
(e) S. M. Levonis, L. F. Bornaghi, T. A. Houston, *Aust. J. Chem.* **2007**, *60*, 821. doi:10.1071/CH07231
(f) S. Manku, D. G. Hall, *Aust. J. Chem.* **2007**, *60*, 824. doi:10.1071/CH07263
(g) P. J. Duggan, D. A. Offerman, *Aust. J. Chem.* **2007**, *60*, 829. doi:10.1071/CH07143
(h) C. D. Roy, H. C. Brown, *Aust. J. Chem.* **2007**, *60*, 835. doi:10.1071/CH07118

[4] M. G. Chudzinski, Y. Chi, M. S. Taylor, *Aust. J. Chem.* **2011**, *64*, 1466.

[5] J. Yoon, A. W. Czarnik, *J. Am. Chem. Soc.* **1992**, *114*, 5874. doi:10.1021/JA00040A067

[6] C. W. Gray, Jr, T. A. Houston, *J. Org. Chem.* **2002**, *67*, 5426. doi:10.1021/JO025876Y

[7] S. Lim, M. Lowry, R. M. Strongin, *Aust. J. Chem.* **2011**, *64*, 1470.

[8] S. Lim, J. O. Escobedo, M. Lowry, R. M. Strongin, *Chem. Commun. (Camb.)* **2011**, 8295. doi:10.1039/C1CC11343G

[9] N. McGregor, C. Pardin, W. G. Skene, *Aust. J. Chem.* **2011**, *64*, 1438.

[10] S. M. Levonis, M. J. Kiefel, T. A. Houston, *Aust. J. Chem.* **2011**, *64*, 1454.

[11] S. M. Levonis, M. J. Kiefel, T. A. Houston, *Chem. Commun. (Camb.)* **2009**, 2278. doi:10.1039/B900836P

[12] J. M. Carr, P. J. Duggan, D. G. Humphrey, E. M. Tyndall, J. M. White, *Aust. J. Chem.* **2011**, *64*, 1417. doi:10.1071/CH11022

[13] H. Nakamura, A. Shoji, A. Takeuchi, H. S. Ban, J.-D. Lee, T. Yamori, S. O. Kang, *Aust. J. Chem.* **2011**, *64*, 1430.

[14] Y. Yamamoto, Y. Takahashi, K. Kurihara, N. Miyaura, *Aust. J. Chem.* **2011**, *64*, 1447.

[15] D. S. Matteson, *Aust. J. Chem.* **2011**, *64*, 1425.

[16] A. Sakakura, T. Ohkubo, R. Yamashita, M. Akakura, K. Ishihara, *Org. Lett.* **2011**, *13*, 892. doi:10.1021/OL102926N

[17] A. Sakakura, R. Yamashita, T. Ohkubo, M. Akakura, K. Ishihara, *Aust. J. Chem.* **2011**, *64*, 1458.

[18] Q. I. Churches, *Aust. J. Chem.* **2011**, *64*, 62. doi:10.1071/CH10341

[19] E. P. Gillis, M. D. Burke, *J. Am. Chem. Soc.* **2007**, *129*, 6716. doi:10.1021/JA0716204.