COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Rhodium-catalysed addition of arylboronic acids to oxabenzonorbornadienes†

Masahiro Murakami* and Hideyuki Igawa

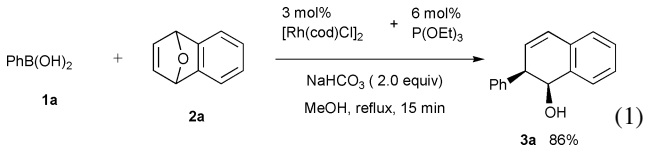
Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Yoshida, Kyoto 606-8501, Japan. E-mail: murakami@sbchem.kyoto-u.ac.jp

Received (in Cambridge, UK) 1st October 2001, Accepted 11th December 2001
First published as an Advance Article on the web 30th January 2002

The facile addition reaction of boronic acids to oxabenzonorbornadienes was achieved using a catalytic amount of a rhodium(I) complex having $P(OEt)_3$ ligands, affording *cis*-2-aryl-1,2-dihydro-1-naphthol stereoselectively, and in good yield without concomitant deboronation of the boronic acid.

The catalysed addition of arylboronic acids to olefins is currently an active research area in organic synthesis. Conjugate addition occurs with electron deficient olefins like enones,[1] alkenylphosphonates,[2] and nitroalkenes.[3] Norbornene undergoes a "merry-go-round"-type multiple alkylation on an aryl group.[4] Aqueous media promotes the addition to styrenyl olefins.[5] On the other hand, the presence of a significant number of bioactive and therapeutically important molecules containing the tetrahydronaphthalene core was the impetus for the development of alkylative ring-opening reactions of oxabenzonorbornadienes with organic halides,[6] arenylstannanes,[7] and organozincs.[8] We report herein on the rhodium-catalysed addition reaction of arylboronic acids to oxabenzonorbornadienes.

Oxabenzonorbornadiene **2a** (1.0 equiv.) was treated with phenylboronic acid **1a** (1.1 equiv.)‡ and $NaHCO_3$ (2.0 equiv.) in the presence of a rhodium complex (0.03 equiv.) prepared *in situ* from $[Rh(cod)Cl]_2$ and $P(OEt)_3$ (Rh : P = 1 : 2) in MeOH at reflux under a nitrogen atmosphere. Under these optimised conditions, the reaction proceeded so quickly that olefin **2a** was completely consumed after only 15 min. Extractive workup followed by chromatographic isolation afforded the ring-opened alcohol **3a** in 86% yield [eqn. (1), Entry 1 of Table 1].



(1)

The *cis* isomer was formed exclusively. This stereochemical outcome parallels the results in alkylative ring-opening reactions[6–8] but is opposite to those of the rhodium-catalysed alcoholysis and aminolysis.[9] Of particular interest was that hydrolytic deboronation of phenylboronic acid was minimized under the present conditions; the use of only 1.1 equiv. of boronic acid **1a** is sufficient to obtain a product yield of 86%, whereas competing hydrolytic degradation reactions demanded the use of an excess of arylboronic acid ranging from 1.4 equiv. up to 10 equiv. in previously reported rhodium-catalysed addition reactions of this type.[1–3,5]

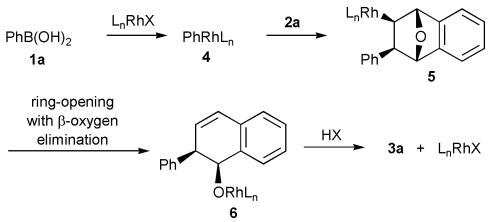
Table 1 Rhodium catalysed coupling of **1a** with **2a**

Entry	Base	Ligand	Solvent	Time	Yield of **3a** (%)
1	$NaHCO_3$	$P(OEt)_3$	MeOH	15 min	86
2	CsF	$P(OEt)_3$	MeOH	20 min	78
3	NEt_3	$P(OEt)_3$	MeOH	20 min	83
4	None	$P(OEt)_3$	MeOH	24 h	14
5	$NaHCO_3$	$P(OMe)_3$	MeOH	15 min	86
6	$NaHCO_3$	$P(OPh)_3$	MeOH	3 h	61 (22)[a]
7	$NaHCO_3$	PPh_3	MeOH	6 h	26 (29)[a]
8	$NaHCO_3$	dppp	MeOH	6 h	43
9	$NaHCO_3$	$P(OEt)_3$	THF	24 h	38

[a] Figures in parentheses refer to yields of 2-phenylnaphthalene.

A detailed examination of the reaction conditions is described in Table 1. While other bases like CsF and triethylamine gave results analogous to that obtained with $NaHCO_3$ (Entries 2 and 3), the reaction in the absence of a base was much slower (Entry 4). As for the phosphorous ligand, an analogous activity was obtained with $P(OMe)_3$ (Entry 5). Other ligands like $P(OPh)_3$, PPh_3, and dppp retarded the reaction and caused the formation of the dehydration product, 2-phenylnaphthalene, with a concomitant decrease in the yield of **3a** (Entries 6–8). The reaction became slower when the methanol solvent was replaced with other solvents like THF (Entry 9).

The following mechanistic scheme explains the formation of **3a** [eqn. (2)]. Initially, phenylrhodium(I) **4** is generated by



(2)

transmetallation of a rhodium(I) species with phenylboronic acid **1a**. This process might be promoted by a base. Then follows the addition of the phenyl–rhodium linkage across a carbon–carbon double bond of **2a** from the *exo*-side to give **5**. β-Oxygen elimination proceeds to open the furyl ring. The resulting rhodium(I) alkoxide **6** undergoes protonolysis with methanol or with phenylboronic acid **1a** to produce the alcohol **3a**.§ The rhodium(I) species regenerated thereby promotes the next catalytic cycle.

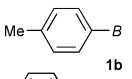
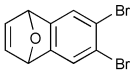
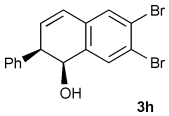
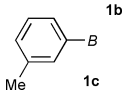
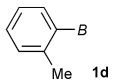
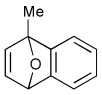
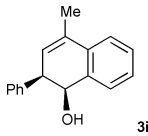
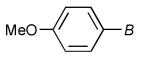
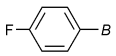
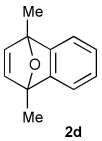
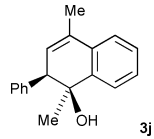
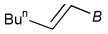
Other examples of the stereoselective synthesis of *cis*-2-aryl-1,2-dihydro-1-naphthol **3** from arylboronic acids **1** and oxanorbornadiene derivatives **2** are listed in Table 2. All isomeric tolylboronic acids, even the sterically congested *o*-isomer **1d** afforded the coupling product in good yield (Entries 1–3). The reaction of (*p*-anisyl)boronic acid **1e** was slower, and an increased amount of the catalyst (0.05 equiv.) was used (Entry 4). An alkenyl group was also successfully transferred onto the oxanorbornadiene core (Entry 6). The bromo–aryl functionality of **2b** was not affected by rhodium (Entry 7).[5] An oxabenzonorbornadiene having one methyl group **2c** worked well (Entry 8), but the reaction of dimethyl-substituted **2d** furnished **3j** in moderate yield, along with other unidentified compounds (Entry 9).

In summary, we have developed a new catalytic process of alkylative ring-opening of oxabenzonorbornadienes with arylboronic acids, in which the serious problem of hydrolytic deboronation of the boronic acid substrate was minimized. The

† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b1/b108808d/

DOI: 10.1039/b108808d

Table 2 The stereoselective synthesis of *cis*-2-aryl-1,2-dihydro-1-naphthol **3**[a]

Entry	$ArB(OH)_2$	**2**	**3** Yield (%)	Entry	$ArB(CH)_2$ **1**	**2**	**3**	Yield (%)
1	 **1b**	**2a**	**3b** 86	7	**1a**	 **2b**	 **3h**	94[b]
2	 **1c**	**2a**	**3c** 90					
3	 **1d**	**2a**	**3d** 88	8	**1a**	 **2c**	 **3i**	91
4	 **1e**	**2a**	**3e** 74[b]					
5	 **1f**	**2a**	**3f** 75	9	**1a**	 **2d**	 **3j**	53[c]
6	 **1g**	**2a**	**3f** 70[c]					

[a] **1** (1.1–1.15 equiv.), **2** (1.0 equiv.), Rh (0.03 equiv.), $NaHCO_2$ (2.0 equiv.) and MeOH (solvent) were used unless otherwise noted. [b] Rh (0.05 equiv.). [c] **1** (2.2–2.3 equiv.), Rh (0.05 equiv.).

examples documented herein provide a promising archetype and broaden the scope of catalysed addition reactions of boronic acids.¶

Notes and references

‡ An aryl boronic acid was used as a mixture with an arylboroxine (dehydrated trimer). The equivalence of **1** was estimated based on the ratio determined by ^{1}H NMR.

§ Direct transmetallation of **6** with the phenyl–boron linkage of **1a** is also conceivable.

¶ *Note added at proof.* Lautens' research group has also been studying the same reaction in an asymmetric form: M. Lautens, Abstract of the post OMCOS-XI symposium: *Thirty years of the cross-coupling reaction*, Kyoto, 2001.

1 (*a*) M. Sakai, H. Hayashi and N. Miyaura, *Organometallics*, 1997, **16**, 4229; (*b*) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai and N. Miyaura, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

2 T. Hayashi, T. Senda, Y. Takaya and M. Ogasawara, *J. Am. Chem. Soc.*, 1999, **121**, 11591.

3 T. Hayashi, T. Senda and M. Ogasawara, *J. Am. Chem. Soc.*, 2000, **122**, 10716.

4 K. Oguma, M. Miura, T. Satoh and M. Nomura, *J. Am. Chem. Soc.*, 2000, **122**, 10464.

5 M. Lautens, A. Roy, K. Fukuoka, K. Fagnou and B. Martin-Matute, *J. Am. Chem. Soc.*, 2001, **123**, 5358.

6 (*a*) C. Moinet and J.-C. Fiaud, *Tetrahedron Lett.*, 1995, **36**, 2051; (*b*) J.-P. Duan and C.-H. Cheng, *Organometallics*, 1995, **14**, 1608; (*c*) C.-C. Feng, M. Nandi, T. Sambaiah and C.-H. Cheng, *J. Org. Chem.*, 1999, **64**, 3538.

7 K. Fugami, S. Hagiwara, H. Oda and M. Kosugi, *Synlett*, 1998, 477.

8 M. Lautens, J.-L. Renaud and S. Hiebert, *J. Am. Chem. Soc.*, 2000, **122**, 1804.

9 (*a*) M. Lautens, K. Fagnou and M. Taylor, *Org. Lett.*, 2000, **2**, 1677; (*b*) M. Lautens, K. Fagnou and T. Rovis, *J. Am. Chem. Soc.*, 2000, **122**, 5650; (*c*) M. Lautens and K. Fagnou, *J. Am. Chem. Soc.*, 2001, **123**, 7170.

Typeset and printed by Black Bear Press Limited, Cambridge, England