Preparation of α-Oxygenated Ketones by the Dioxygenation of Alkenyl Boronic Acids**

Aditi S. Patil, Dong-Liang Mo, Heng-Yen Wang, Daniel S. Mueller, and Laura L. Anderson*

The ubiquitous use of aryl, alkenyl, and alkyl boronic acids for the formation of new C-C, C-N, and C-O bonds in crosscoupling reactions is indicative of the importance of these compounds in organic synthesis.^[1] Although the use of boronic acids for the preparation of a variety of new bonds is well established, we were interested in testing if the reactivity of alkenyl boronic acids could be further diversified to include dioxygenation and the synthesis of α -oxygenated ketones. The conversion of alkenyl boronic acids to α -oxygenated ketones would provide a unique retrosynthetic disconnection for the preparation of complicated targets containing these challenging motifs.^[2-8] Towards the goal of alkenyl boronic acid dioxygenation, we hypothesized that etherification of an alkenyl boronic acid with N-hydroxyphthalimide would form an N-enoxyphthalimide poised to undergo a [3,3] rearrangement to give an α -oxygenated ketone (Scheme 1). This method would avoid the use of



Scheme 1. Dioxygenation of alkenyl boronic acids. OAc = acetate, PhthN = phthalimide.

highly reactive electrophilic oxygenation reagents, not require the preparation of α -halogenated precursors, and allow access to linear α -oxygenated ketones from internal alkynes.^[4,5d,7–9] Moreover, the nature of the transition state of the pericyclic reaction would allow for potential diastereoselective construction of the α -oxygenated stereocenter. Herein, we describe the development of a new method for the dioxygenation of alkenyl boronic acids through a copper-

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mediated etherification of *N*-hydroxyphthalimide followed by a [3,3] rearrangement to provide α -hydroxy or α -benzoyloxy ketones in two high-yielding steps from simple starting materials.

Our efforts towards achieving the dioxygenation of alkenyl boronic acids began with the optimization of conditions for the cross-coupling of alkenyl boronic acids and N-hydroxyphthalimide to form N-enoxyphthalimides. Although the copper-mediated arylation of N-hydroxyphthalimide with aryl boronic acids is known, to the best of our knowledge, the corresponding process for vinylation has not yet been reported.^[10-12] Mixtures of copper salts, bases, and dessicants, as well as equivalents of reagents, were screened for their effectiveness in promoting the desired coupling of 1 and 2a. As shown in entries 1-4 of Table 1, the use of 2 equiv of boronic acid 2a provided a higher yield of 3a for both copper-mediated and copper-catalyzed transformations, although the difference in reaction efficiency was more striking for the catalytic process.^[13] The greater sensitivity of the catalytic reaction to changes in reaction conditions was consistent throughout the optimization process and guided our inquiry. $Cu(OAc)_2$ (OAc = acetate) was shown to be the

 Table 1:
 Optimization of the etherification of N-hydroxyphthalimide with

 2-butenyl boronic acid.
 1

	О Ме N-OH [Cu] (1 еquiv base (3 еquiv), N DCE, 25	B(OH) ₂ Me 2a or 20 mol %) Ia ₂ SO ₄ (4 equi °C, air		N-OMe Me 3aMe
Entry	[Cu]	[2 a]	Base	Yield [%] of 3 a ^[a]
1	Cu(OAc) ₂ (1 equiv)	1 equiv	pyridine	71
2	$Cu(OAc)_2$ (1 equiv)	2 equiv	pyridine	96
3	Cu(OAc) ₂ (20 mol%)	1 equiv	pyridine	6
4	Cu(OAc)₂ (20 mol%)	2 equiv	pyridine	87
5	CuCl (20 mol%)	2 equiv	pyridine	7
6	Cul (20 mol%)	2 equiv	pyridine	78
7	Cu(TFA) ₂ (20 mol%)	2 equiv	pyridine	61
8	Cu(OTf) ₂ (20 mol%)	2 equiv	pyridine	8
9	CuTC (20 mol%)	2 equiv	pyridine	81
10	Cu(OAc) ₂ (20 mol%)	2 equiv	NEt ₃	68
11	Cu(OAc) ₂ (20 mol%)	2 equiv	DABCO	NR
12	Cu(OAc) ₂ (20 mol%)	2 equiv	imidazole	NR
13	Cu(OAc) ₂ (20 mol%)	2 equiv	KOtBu	NR

[a] Yields were determined by ¹H NMR spectroscopy using 1,3,5trimethoxybenzene as an internal standard; NR = no reaction. DABCO = 1,4-diazabicyclo[2.2.2]octane, DCE = 1,2-dichloroethane, OAc = acetate, TC = 2-thiophenecarboxylate, Tf = trifluoromethanesulfonate, TFA = trifluoroacetate.

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optimal catalyst when compared to other Cu^I and Cu^{II} salts (entries 5-9) and pyridine was shown to be the optimal base when compared to other amines and inorganic bases (entries 10-13). Neither the coppermediated nor the copper-catalyzed coupling reaction showed any conversion to the desired product when run in the absence of air, and both transformations required the use of a halogenated solvent. The crosscoupling process was fairly insensitive to the choice of desiccant; 4 Å molecular sieves and MgSO₄ gave the desired product in only slightly attenuated yields.^[14] The optimization study concluded that treatment of a 1:2 mixture of 1/2a in 1,2dichloroethane (DCE) with Cu-(OAc)₂ (1 equiv or 20 mol %), pyri- $(3 \text{ equiv}), \text{ and } Na_2SO_4$ dine (4 equiv) in air provided optimal conversion of 2a to 3a.

4

7

9

1

With the optimal conditions for the cross-coupling of 1 and 2a in hand, the scope of the transformation was evaluated with a variety of alkenyl boronic acids to determine the tolerance for boronic acid substitution patterns. As shown in Table 2, both copper-mediated and copper-catalyzed conditions converted 1- and 2-trans-substituted vinyl boronic acids, Z-disubstituted alkenyl boronic acids, and cyclic alkenyl boronic acids to the desired N-enoxyphthalimides 3 with retention of alkene geometry.^[15] Both alkyl- and aryl substituents were tolerated for the boronic acid coupling partner, as were common aryl electron-withdrawing functional groups such as nitro, fluoro, and trifluoromethyl, as well as common

 Table 2:
 Scope of the etherification of N-hydroxyphthalimide with alkenyl boronic acids.

	N-OH 0 1	R ² R ¹ 2 <u>Cu(OAc)₂ (1 equiv or 20</u> pyr (3 equiv), Na ₂ SO ₄ (4 DCE, 25 °C, air	i mol %) –6 equiv)		
Entry	Product	Yield [%] of 3 ^[a]	Entry	Product	Yield [%] of 3 ^[a]
1	PhthN-OMe 3aMe	98 ^[b] (76)	12	PhthN $-O$ Ar 3I nBu Ar = p -CF ₃ (C ₆ H ₄)	82 (73)
2	PhthN-O 3b <i>n</i> Bu	81 (70)	13	PhthN-O 3m	83 (76)
3	PhthN-O 3c	87 (74)	14	PhthN-O 3n	73 (68)
4	PhthN-O 3d Ph	88 (78)	15	PhthN-O 30 O	91 (89)
5	PhthN-O_C ₅ H ₁₁ 3e C ₅ H ₁₁	81 (77)	16	PhthN-O 3p	86 (82)
6	PhthN-O 3f	47	17	PhthN-O 3q Me	84 (78)
7	PhthN-O Ph 3g	86 (77)	18	Me PhthN-O 3r	41
8	PhthN-O Ph 3h Et	76 (67)	19	PhthN-O 3s	86 (80)
9	PhthN $-O$ Ar 3i nBu Ar = p -Me(C ₆ H ₄)	63 (66)	20	PhthN-O 3t	64
10	PhthN=O Ar 3j $nBuAr = p-NO_2(C_nH_a)$	67 (55)	21	PhthN-O 3u	83
11	PhthN=O Ar 3k nBu Ar = p-F(C ₆ H ₄)	70 (71)	22	PhthN-O 3v	76 (52)

[a] Yield of isolated product using 1 equiv Cu(OAc)₂ and (yield of isolated product using 20 mol% Cu(OAc)₂). [b] When run on a 1 mmol scale, the yield of isolated product using 1 equiv of Cu(OAc)₂ was 74%. Cy = cyclohexyl, DCE = 1,2-dichloroethane, PhthN = phthalimide, OAc = acetate, pyr = pyridine.

protecting groups such as ketals. Trisubstituted alkenyl boronic acids and alkenyl boronic acids with ortho-substituted aryl groups currently represent a limitation of this method. Unfavorable steric interactions also hinder the etherification of 6-methyl cyclohexenyl boronic acid 2r; however, no similar inhibition was observed for the fused system 2v. The broad scope of the copper-mediated cross-coupling of N-hydroxyphthalimide 1 and alkenyl boronic acids 2 ultimately provided an array of N-enoxyphthalimides 3 to screen for the [3,3] rearrangement.

Solutions of N-enoxyphthalimides 3 in C_6D_6 or toluene were heated at 80-90°C for 10-16 h to promote a [3,3] rearrangement and afford dioxygenated alkenyl boronic acids as imidates 4. These rearrangements occurred in almost quantitative yields, as determined by comparison to an internal standard by ¹H NMR spectroscopy; however, imidates 4 were unstable when subjected to silica gel chromatography.^[16] Isolation and purification of α -hydroxy ketones 5 was achieved in high yield after the hydrolysis of crude samples of 4 (Table 3). An ion-exchange resin provided optimal yields for the cleavage of phthalimide from 4, but silica gel was similarly effective with longer reaction times. a-Hydroxyketones 5 that were too volatile or hydrophilic to be separated from phthalimide by extraction were protected in solution and isolated as the corresponding α -benzoyloxy ketones 6 (Table 3). The N-enoxyphthalimides 3b-3d, underwent rearrangements to form α -oxygenated aldehydes **4b**-**4d**, which were isolated without further purification as the

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Table 3: Preparation of α -hydroxy- and α -benzoyloxyketones by rearrangement and hydrolysis of N-enoxyphthalimides 3.



[[]a] Yield of isolated product. [b] Hydrolysis promoted with SiO₂. Bz=benzoyl, Amberlite=Amberlite IR120H, ion-exchange resin.

corresponding imidates to avoid polymerization of the corresponding α -hydroxy aldehydes [Eq. (1)]. The products shown in Table 3 and equation 1 describe the broad scope of α -oxygenated carbonyl compounds that can be prepared from the dioxygenation of alkenyl boronic acids with N-hydroxyphthalimide 1 through the rearrangement of N-enoxyphthalimides 3. This method provides a valuable alternative to

R = *n*Bu, 90 °C, **4b**, 67% cyclohexyl, 90 °C, **4c** Ph, 50 °C, **4d**, 76%

4c. 73%

known procedures, which originate from ketone or aldehyde starting materials and employ electrophilic sources of oxygen.

Several aryl-substituted Nenoxyphthalimides exhibited exceptions to the general thermal reactivity patterns depicted in Table 3 and equation 1 that suggested trends in the [3,3] rearrangement activity of these compounds. *N*-Enoxyphthalimide **3d** readily formed 4d when heated to only 50°C [Eq. (1)]. This transformation is in contrast to 3b and 3c, which rearranged at 90°C, and 3g, which exhibited no rearrangement reactivity even when heated to 130°C. The combination of an aryl group at the 1-position of N-enoxyphthalimides 3h-3l, and an alkyl group at the 2-position attenuated the opposing affects observed for 3d and 3g, and the rearrangements to afford 4h-41 occurred at 80°C (Table 3); however, the addition of an electron-donating group to the aryl ring once again reduced the rearrangement temperature to 25-50°C to give 5w [Eq. (2)]. N-Enoxyphthalimide 3w could not be isolated, as the copper-mediated coupling provided a 2:1 mixture of 3w/5w. Filtration of this mixture through silica gel to remove Cu-(OAc)₂, followed by warming to 50°C for 10 h and hydrolysis, gave 5w in 57% yield over three steps. A similarly efficient process was also observed for the transformation of 2a to 6a in 67% yield with no formal purification of intermediates, only the removal of $Cu(OAc)_2$ prior to rearrangement [Eq. (3)].



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3

heat

 $C_6 D_6$

sealed tube

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 $Cu(OAc)_2$ can be present in substoichiometric amounts during the rearrangement of **3a**, but attenuated yields of **4a** are obtained. These results show that the [3,3] rearrangement of **3** is inhibited by the presence of copper salts and facilitated by electron-donating aryl groups at the 1-position and phenyl substituents at the 2-position of the enol ether.

The diastereoselectivity of the [3,3] rearrangement of *N*enoxyphthalimides was tested using *N*-enoxyphthalimides 3q-3u, which are derived from substituted cyclohexenyl boronic acids. Compounds 3q, 3s, 3t, and 3u underwent [3,3] rearrangements to give 50:50 to 60:40, *cis/trans* diastereomeric mixtures of 4 and subsequent hydrolysis to give 6q, 6s, and 5t with no significant change in the diastereomeric ratio (Table 3). Hydrolysis and protection of 4u epimerized the α benzoyl group, resulting in a 75:25 mixture of *cis/trans* 6u(Table 3). Surprisingly, the rearrangement of 3r strongly favors formation of the *trans* diastereomer (Scheme 2). We



Scheme 2. Diastereoselective rearrangement of 3r to 4r.

assume that this result is due to minimization of steric interactions as the rearrangement occurs via a chair transition state (TS1). In contrast to 4-substituted cyclohexenyl substrates 3q, 3s, and 3u, rotation to give an approach of the carbonyl oxygen from the higher energy twist conformation and provide the *cis* diastereomer is inaccessible for **3r** because of the 6-methyl substituent, which inhibits rotation of the Nenoxyphthalimide around the C-O bond. A moderate increase in the cis/trans ratio from 15:85 to 20:80 was observed upon hydrolysis and protection of 4r. To the best of our knowledge, the diastereomeric ratio observed for 4r represents the highest observed in favor of the trans isomer for 2-methylcyclohexanone α -oxygenation.^[4d,17] This implies that the dioxygenation of alkenyl boronic acids may not only provide a new retrosynthetic disconnection for the preparation of a-oxygenated carbonyl compounds, but also access to relative stereochemical patterns not readily available through enolate oxidation procedures.

The diastereoselectivity observed for the rearrangement of **3r** suggested that the [3,3] rearrangements of *N*-enoxyphthalimides proceed by a unimolecular pericyclic reaction. The intramolecular nature of the transition state was further supported by a crossover experiment using *N*-enoxyphthalimides **3b** and **7** [Eq. (4)]. When a 1:1 mixture of these compounds was heated in C_6D_6 at 90 °C for 18 h, only **4b** and **7** were observed and there was no evidence of crossover by ¹H



or ¹³C NMR spectroscopy. To investigate the possibility of a radical reaction pathway, a radical clock experiment was tested with *N*-enoxyphthalimide **3 f**. Upon heating **3 f** in either the presence or the absence of Bu₃SnH, no indication of the formation of an α , β -unsaturated aldehyde was observed, suggesting that the [3,3] rearrangement occurs through a twoelectron pathway.

In summary, we have shown that dioxygenation of alkenyl boronic acids **2** with *N*-hydroxyphthalimide **1** can be achieved by a two-step process involving copper-mediated etherification to form an *N*-enoxyphthalimide **3** and a subsequent [3,3] rearrangement to provide α -hydroxy ketones **5** or α -benzoyloxy ketones **6**, after hydrolysis of the phthalimide imidate. This transformation provides a new retrosynthetic disconnection for the preparation of α -oxygenated carbonyl compounds that does not require the use of a highly reactive electrophilic oxygen source or a carbonyl compound as a starting material. Ongoing work in our laboratory is focused on further exploring the synthetic utility of this transformation and exploiting the observed diastereoselectivity.

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Communications



Pericyclic Rearrangement

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Preparation of α -Oxygenated Ketones by the Dioxygenation of Alkenyl Boronic Acids



Two in two: Dioxygenation of alkenyl boronic acids has been achieved with *N*hydroxyphthalimide. The two-step process involves etherification of an alkenyl boronic acid with *N*-hydroxyphthalimide followed by a [3,3] rearrangement. The dioxygenated product can then be hydrolyzed to form either the corresponding α -hydroxy ketone or the α -benzoyloxy ketone.

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