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Double Hydroboration of Quinolines *via* Borane Catalysis: Diastereoselective One Pot Synthesis of 3-Hydroxytetrahydroquinolines

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Dedicated to Professor Eric N. Jacobsen on the occasion of his 60th birthday

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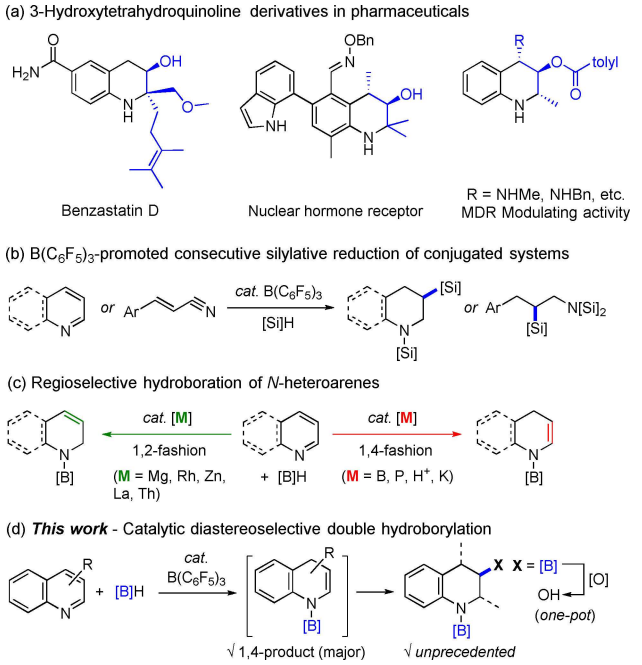
Abstract: Described herein is an organoborane-catalysed consecutive borylative reduction of quinolines and isoquinolines to furnish tetrahydro(iso)quinolines bearing a C(sp^3)–B bond β to the nitrogen atom. The installed C–B bond is oxidatively transformed to the hydroxy group in one pot. The present double hydroboration is proposed to proceed *via* a stepwise ionic mechanism involving a boronium ion. The stereo-outcome was found to be dependent on the position (C2 *vs* C4) of the substituents in quinolines.

Keywords: Lewis acidic borane; hydroboration; consecutive reaction; ionic mechanism; diastereoselectivity

Tetrahydroquinolines are a prevalent synthetic motif in numerous biologically active natural products and pharmaceutical compounds (Scheme 1a).[1] As a result, there have been considerable interests in the development of efficient and selective catalytic routes to tetrahydroquinolines and their derivatives.[2] Hydrogenation of quinolines is undoubtedly the most straightforward and atom-economic approach to access tetrahydroquinolines.[3] However, this procedure often leads to exhaustively reduced products with inferior functional group tolerance, thus limiting the resultant molecular diversity in the reduced *N*-heterocyclic products to serve as a synthetic intermediate. In this regard, reduction of *N*-heteroaromatics with hydrosilanes is an attractive alternative[4] mainly because the stoichiometric amounts of reductants, hydrosilanes, can be precisely added. Moreover, an additional synthetic benefit of this hydrosilane reduction approach can be achieved in that a silyl group can be incorporated into products by forming a new C–Si bond during the course of the reductive process. Indeed, our group recently reported the $B(C_6F_5)_3$-catalyzed silylative reduction of pyridines, quinolines, and α,β-unsaturated nitriles and imines to afford C(sp^3)–Si moiety-containing products (Scheme 1b).[5]

On the other hand, a number of elegant catalytic hydroboration methodologies for generating six-membered *N*-heteroarenes have been developed by using organohydroboranes such as pinacolborane to selectively afford *N*-borylated 1,2- or 1,4-dihydro-products (Scheme 1c).[6] For example, *in situ* generated metal hydride species based on Mg, Rh, Zn, La, and Th were found to promote 1,2-hydroboration of pyridines[6a–f] while 1,4-selectivity was observed *via* an ionic outer-sphere pathway catalysed by Lewis or Brønsted acids.[6g–m] Despite these recent advances in the dearomative hydroboration of *N*-heteroarenes, to our best knowledge, no catalytic procedures have been revealed thus far for the sp^3 C–B bond-forming hydroboration of *N*-heteroaromatics.[7]

Herein we report a $B(C_6F_5)_3$-catalyzed double hydroboration of quinolines to give rise to β-borylated tetrahydroquinolines (Scheme 1d). It represents the first catalyst system toward consecutive borylative reduction of quinolines. This transition metal-free borane catalysis was found to proceed *via* a stepwise ionic mechanism, which eventually leads to 2,3-*cis* or 3,4-*trans* products depending on the substituent's position on the *N*-aromatic skeleton.

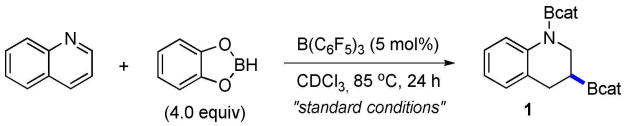


Scheme 1. 3-Hydorxytetrahydroquinolines as a structural motif of pharmaceutical drugs and $B(C_6F_5)_3$-catalyzed dearomative hydroboration reactions.

At the outset, we performed optimization studies for the presupposed $B(C_6F_5)_3$-catalyzed consecutive borylative reduction of quinoline (Table 1). The desired double hydroboration took place with 4 equiv. of catecholborane (HBcat) in the presence of $B(C_6F_5)_3$ catalyst (5 mol%) at 85 °C in $CDCl_3$, thus providing 1,3-*bis*-borylated tetrahydroquinoline **1** in 82% NMR yield after 24 h (entry 1).[8] Based on the fact that frustrated Lewis pairs are capable of activating a B–H bond of organohydroboranes,[9] catalytic reactions in the presence of Lewis bases were examined (entries 2–3). A catalytic amount of PPh_3 did not bring any change in yielding **1** (entry 2) while another Lewis base DABCO led to slightly decreased reaction efficiency (entry 3). A reaction in benzene instead of chloroform caused a significant decrease in yield of **1** (entry 4). When the reaction was conducted at 25 °C, the desired product was obtained in 77% (entry 5) while it remained rather similar even at higher temperature (110 °C, entry 6 *vs.* 1).

Notably, the identity of hydroboranes was shown to be more critical as evidenced by the inferior yield with HBpin instead of HBcat (entries 1 *vs.* 7). The decrease of HBcat quantity to 2.2 equiv. still gave **1** in good yield (entry 8), while treating a stoichiometric amount of HBcat generated a mixture of 1,2- and 1,4-dihydroquinolines, and product **1** was not formed (entry 9). Noteworthy is that a reaction for a short time (0.5 h) furnished not only **1** (44%) but also a mixture of 1,4-(37%) and 1,2-(9%) dihydroquinolines under

Table 1. Optimization of Reaction Conditions.[a]



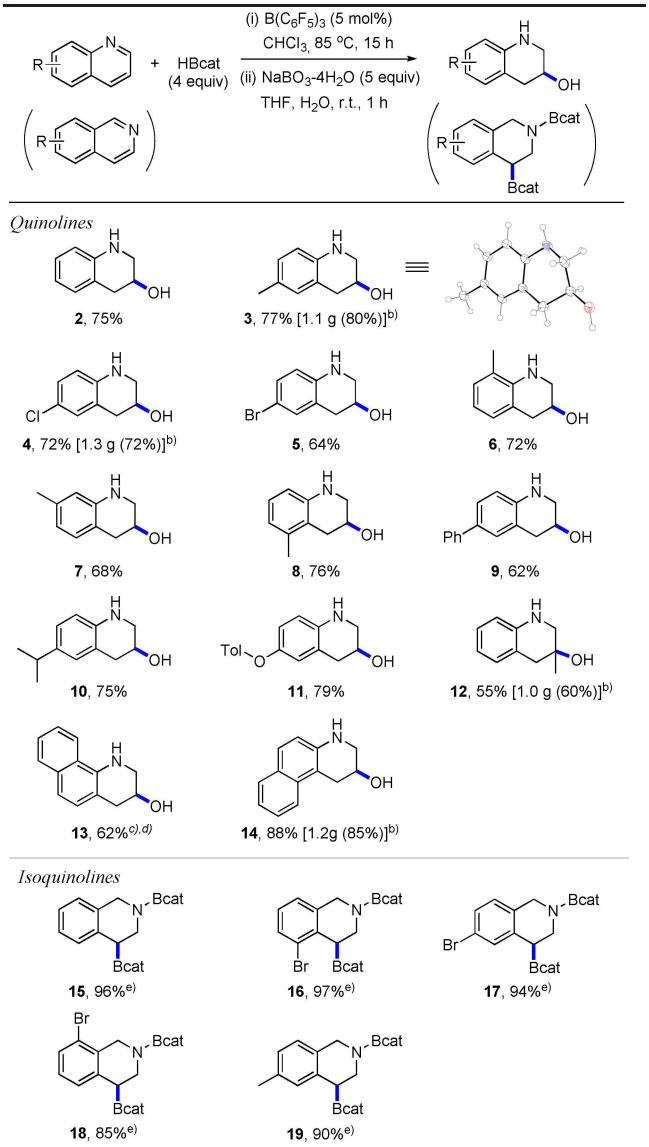
entry	changes from the "standard conditions"	Yield of **1** (%)[b]
1	None	82
2	Addition of PPh_3 (5 mol%)	80
3	Addition of DABCO (5 mol%)	70
4	C_6D_6 instead of $CDCl_3$	60
5	25 °C instead of 85 °C	77
6	110 °C instead of 85 °C	79
7	HBpin instead of HBcat	38
8	HBcat (2.2 equiv.) instead of HBcat (4.0 equiv.)	80
9	HBcat (1.1 equiv.) instead of HBcat (4.0 equiv.)	< 1 (87)[c]
10	0.5 h instead of 24 h	44 (46)[d]

[a] Reactions were carried out in 0.5 mmol scale in a J. Young NMR tube. Conversion of quinoline in all entries was quantitative.
[b] Determined by ^{1}H NMR of the crude reaction mixture on the basis of 1,1,2,2-tetrachloroethane (TCE) as an internal standard.
[c] Combined yield of dihydroquinolines: [1,2-(20%)/1,4-(67%)].
[d] [1,2-(9%)/1,4-(37%)].

otherwise same conditions (entry 10). The formation of two regioisomers suggests that the initial step likely involves 1,2-hydroboration as a competing hydride transfer path.

Under the optimized conditions, the borylative reduction of quinolines substituted on the benzofused ring was first investigated (Table 2).[10] The initially formed 1,3-*bis*-borylated tetrahydroquinolines were converted to the 3-hydroxytetrahydroquinolines upon the one-pot oxidation with sodium perborate tetrahydrate. Quinolines with alkyl, aryl, or halide groups at the C5 to C8 positions were found to display minimal impact on the formation of the desired β-borylated products (**2**–**10**). An ethereal sp^2 C–O bond (aryloxy group) was tolerated under the present reductive conditions to give the product **11** in 79% yield. The current catalysis proved to have high fidelity towards sp^3 C–B bond formation at the β-position to give the C3-borylated tetrahydroquinoline possessing a newly formed *tetra*-substituted carbon (**12**). Two isomeric benzoquinolines underwent the borylative reduction with similar efficiency (**13**–**14**). It needs to be emphasized that the present metal-free catalytic system operates even in the gram-scale reaction with good efficiency (for **3**, **4**, **12**, and **14**: 60–85%).

Table 2. Substrate Scope of Quinolines.[a]

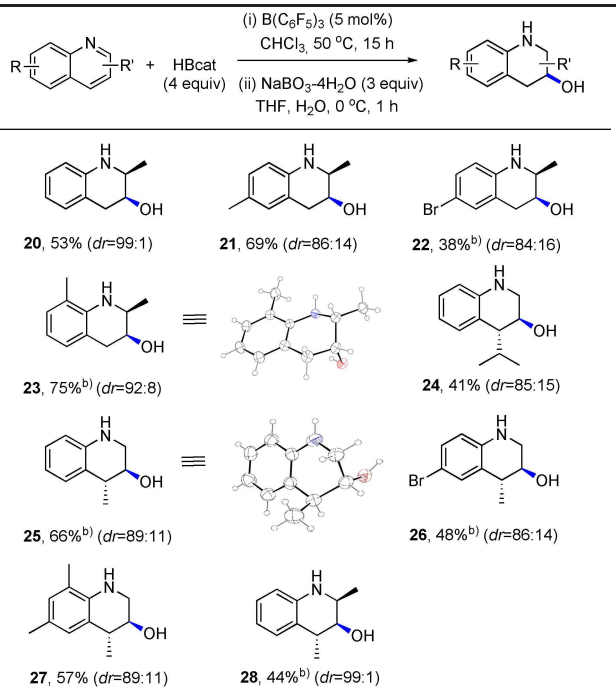


[a] Reaction condition: substrate (0.5 mmol), HBcat (2.0 mmol) and $B(C_6F_5)_3$ (5 mol%) in $CHCl_3$ (0.5 mL) at 85 °C for 15 h: isolated yields.
[b] Gram-scale synthesis.
[c] $NaBO_3$–$4H_2O$ (3 equiv.) was used.
[d] At 50 °C.
[e] Determined by ^1H NMR of the crude reaction mixture on the basis of 1,1,2,2-tetrachloroethane (TCE) as an internal standard.

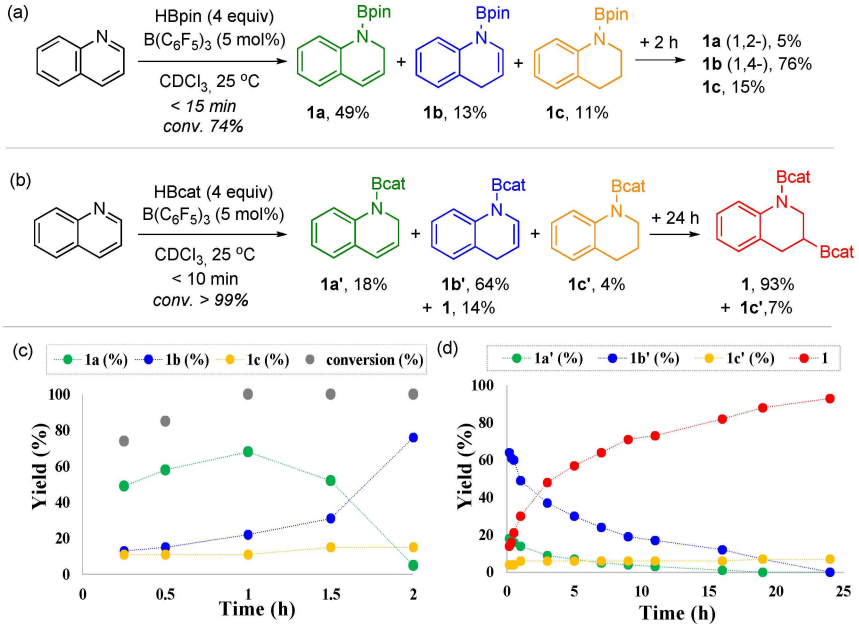
Gratifyingly, a range of isoquinolines bearing substituents at the benzene ring also underwent smoothly the consecutive borylation at 85 °C to provide the corresponding 2,4-*bis*-borylated tetrahydroisoquinolines in high yields (**15**–**19**). It is interesting to note that when compared to the present borylative conversion, the *silylative* reduction of isoquinolines was operative only under rather harsher conditions (100 °C, 24 h), thus giving moderate yields of β-silylated azacyclic products.[5a]

Next, we were curious to see whether a diastereoselective transformation can be achieved by subjecting quinolines having substituent(s) at the C2 and/or C4 positions (Table 3). To obtain better diastereoselectivity in case when it is, reactions were conducted at slightly lower temperature (50 °C for 15 h) in the presence of 5 mol% of $B(C_6F_5)_3$. To our delight, 2-methylquinoline was converted to the corresponding β-hydroxyl product (**20**) in 53% with excellent diastereomeric ratio (*dr* = 99:1). The initially formed β-borylated intermediate was oxidized in a stereo-retentive manner.[11] As observed in the $B(C_6F_5)_3$-catalyzed silylative reduction,[5a] the stereo-relationship of **20** between the preexisting methyl and a newly formed C (sp^3)–B bond was determined to be *cis*. In addition, reactions of 2-methylquinolines substituted with methyl or halide groups at the benzofused ring also afforded the corresponding *cis*-isomeric products mainly although stereoselectivity was observed to be slightly decreased (for **21**–**23**: *dr* = 84:16–92:8).[12] On the other hand, 4-substituted quinolines were initially reduced in a *trans*-manner and then the β-borylated intermediates were oxidized to *trans*-3-hydroxyteter-

Table 3. Diastereoselective Borylative Reduction.[a]



[a] Reaction condition: substrate (0.5 mmol), HBcat (2.0 mmol) and $B(C_6F_5)_3$ (5 mol%) in $CHCl_3$ (0.5 mL) at 50 °C for 15 h: isolated yields. Diastereomeric ratio (*dr*) was determined by ^1H NMR analysis of the catalytic crude reaction mixture.
[b] $NaBO_3$–$4H_2O$ (5 equiv.) was used.

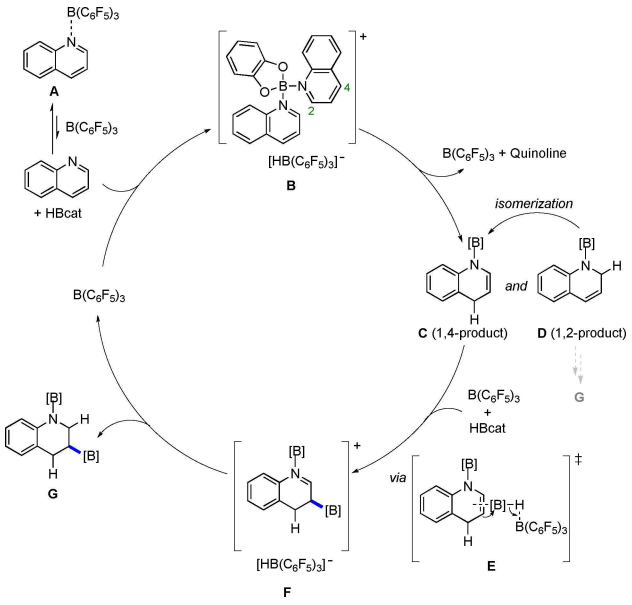


Scheme 2. [1]H NMR-reaction progress monitoring.

ahydroquinolines (**24**–**27**: *dr* = 85:15–89:11). Notably, when 2,4-dimethylquinoline was subjected to the standard conditions, a consecutive borylation occurred to give the desired β-hydroxy product **28** in excellent diastereoselectivity (*dr* = 99:1). In this reaction, the boryl transfer step is assumed to determine the stereorelationship between the C4-methyl and the incorporated C–B moiety while the relative stereochemistry between the C2-methyl and the C–B bond is proposed to be determined at the hydride transfer step by $[HB(C_6F_5)_3]^-$. These mechanistic implications underline a stereoselective sequential transfer of the boryl and hydride groups under the current borane catalysis.

To gain more insights, the consecutive hydroboration of quinoline with excessive HBpin or HBcat were monitored at 25 °C by [1]H NMR (Scheme 2). In 15 min, the reaction with HBpin as a reducing agent showed 74% conversion to provide a mixture of dihydroquinolines and teterahydroquinoline, wherein 1,2-intermediate (**1a**) was 49% and 1,4-intermediate (**1b**) was 13%. Upon prolonged reaction time (2 h), a full conversion was observed to give only 5% of **1a** along with 76% of **1b**. Such a notable change in the ratio of **1a** to **1b** during the course of reaction progress suggests that an isomerization of 1,2-intermediate takes place to lead to the thermodynamically more favoured 1,4-intermediate (Scheme 2a,c).[13] Interestingly, the use of HBcat resulted in a faster reaction, thus reaching a quantitative conversion in 10 min giving 1,4-intermediate as a major component (**1b′**, 64%) along with β-borylated tetrahydroquinoline **1** in 14%. This mixture was converted eventually to **1** in 93% yield in 24 h. This result again may corroborate our working proposal that an *isomerization* of 1,2-intermediate (**1a′**) occurs leading to 1,4-isomer (**1b′**) during the reaction progress (Scheme 2b,d).

Based on the previous reports and the present mechanistic insights, we propose an outer-sphere ionic pathway for the present consecutive hydroboration of quinolines involving a boronium ion as a key species (Scheme 3).[6g,14–15] Initially, $B(C_6F_5)_3$ forms a quinoline



Scheme 3. Proposed mechanism.

adduct **A** as an off-cycle resting species[5,16] and the constructive path begins upon the activation of a B–H bond of HBcat by $B(C_6F_5)_3$ to generate a boronium ion pair bearing a borohydride anion **B**. It is postulated that the subsequent hydride transfer from the $[HB(C_6F_5)_3]^-$ species occurs mainly at the C4-position of the bound quinoline to afford 1,4-intermediate **C**. In sequence, this 1,4-adduct **C** undergoes a turnover-limiting C3-selective hydroboration to liberate a borylated tertrahydroquinoline **G** presumably *via* an iminium intermediate **F**. As mentioned above, an initially formed allylamine adduct **D** will be isomerized to its 1,4-isomer **C** although detailed pathways are not known at the present stage.[17]

In summary, we have developed the $B(C_6F_5)_3$-catalyzed borylative reduction of quinolines with a new sp^3 C–B bond formation at the C3-position. The resultant 1,3-*bis*-borylated tetrahydroquinolines are converted to 3-hydroxytetrahydroquinolines by an one-pot oxidation. An ionic stepwise pathway involving a boronium species is proposed that enables the diastereoselective dearomative borylation cascade. This metal-free catalytic procedure is anticipated to offer an access to pharmaceutically interesting β-hydroxy-tetrahydro- quinolines from quinolines in a stereoselective manner.

Experimental Section

General Procedure

step 1) In a 2.5 mL reaction vial, catecholborane (2.0 mmol, 4.0 equiv.) was added to a solution of $B(C_6F_5)_3$ (5.0 mol%) in $CHCl_3$ (0.5 mL) under Ar atmosphere. Quinoline (0.50 mmol) was then added, and the reaction mixture was stirred at 85 °C for 15 h. After completion of the reaction, the mixture was allowed to cool down to room temperature and concentrated under reduced pressure.

step 2) To the above crude reaction mixture dissolved in THF (2.0 mL) and H_2O (2.0 mL) was added sodium perborate tetrahydrate (2.5 mmol, 5.0 equiv.). Then, the mixture was stirred at room temperature for 1 h. The mixture was concentrated under reduced pressure and diluted with H_2O (10 mL). The resulting solution was extracted with EtOAc (10 mL × 3) and the combined organic layers were washed with brine (30 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/*n*-hexane, 1/1) to give the corresponding 3-hydroxytetrahydroquinoline products.

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[17] Oestreich reported a Lewis acidic borane-promoted hydroboration of styrenes, wherein $B(C_6F_5)_3$ catalyst did not enable β-selective hydroboration of styrene substrates. This result may support our assumption that the 1,2-adduct in our case is not directly reduced to the final product of β-borylated tetrahydroquinoline such as G during the catalysis, see: Q. Yin, S. Kemper, H. F. T. Klare, M. Oestreich, *Chem. Eur. J.* **2016**, *22*, 13840–13844.

[18] CCDC numbers for compounds 3 (1952314), 23 (1941403), and 25 (1941402) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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