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Metal-Free Borane-Catalyzed Highly Stereoselective Hydrogenation of Pyridines

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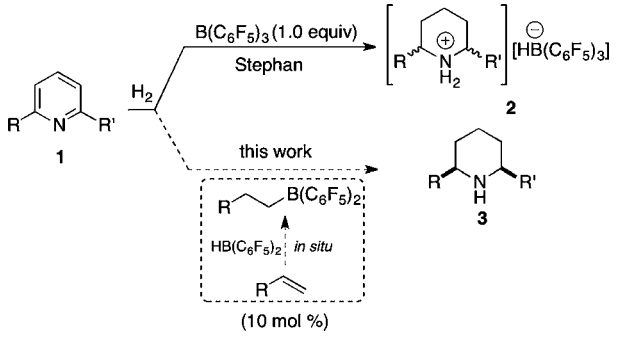
Supporting Information

ABSTRACT: A metal-free direct hydrogenation of pyridines was successfully realized by using homogeneous borane catalysts generated from alkenes and $HB(C_6F_5)_2$ via in situ hydroboration. The reaction affords a broad range of piperidines in high yields with excellent cis stereoselectivities.

Piperidines are very important moieties contained in a wide range of biologically active compounds, and numerous methodologies have been established for their synthesis.[1] The catalytic hydrogenation of pyridines with H_2 undoubtedly provides a simple and straightforward approach for accessing piperidines, although it is essential to overcome some inherent challenges presented by catalyst deactivation and pyridine dearomatization.[2] Various heterogeneous transition-metal catalysts and several homogeneous Rh, Ir, and Ru complexes have been studied for the direct hydrogenation of pyridines, but harsh reaction conditions and/or specific pyridines bearing activating groups are often required because of the low activity and selectivity of the catalysts.[3,4] Recently, an organocatalytic transfer hydrogenation for partial reduction of electron-deficient pyridines with Hantzsch esters was also reported.[5] Moreover, the hydrogenation of relatively more reactive pyridine derivatives such as pyridinium salts, pyridine *N*-oxides, and *N*-iminopyridium ylides using either heterogeneous or homogeneous catalysts provides an alternative and efficient strategy for the synthesis of piperidines.[6,7] Despite these advances, the direct hydrogenation of pyridines is still a challenge. In particular, metal-free catalytic hydrogenation of simple pyridines is of great interest and has rarely been reported.

The lately emerging frustrated Lewis pairs (FLPs) have become one promising class of catalysts for metal-free homogeneous hydrogenation.[8,9] A broad range of substrates, including imines,[10] N-heterocycles,[11] nitriles,[10a] alkenes,[10b,c,h,i,12] and so on,[13] can be efficiently hydrogenated under the catalysis of FLPs. In particular, Stephan and co-workers achieved an amazing aromatic hydrogenation of anilines with 1.0 equiv of $B(C_6F_5)_3$ to afford cyclohexylamine derivatives.[13d] Very recently, Stephan and co-workers also described an interesting example of the reduction of pyridines **1** under H_2 using a stoichiometric amount of $B(C_6F_5)_3$ to furnish piperidinium salts **2** (Scheme 1).[14] The replacement of one pentafluorophenyl group of $B(C_6F_5)_3$ by other groups (e.g., mesityl and alkenyl by Soós[10h,11b] and Erker,[13c] respectively) provided a number of efficient FLP catalysts for hydrogenation.[9] Previously, we accomplished a highly enantioselective hydrogenation of imines using catalysts generated in situ by hydroboration of alkenes with $HB(C_6F_5)_2$.[15,16] We envisioned that this strategy would also provide a good opportunity to develop the challenging metal-free catalytic hydrogenation for simple pyridines, especially for 2,6-disubstituted pyridines, which are often inert substrates in the reported work (Scheme 1). Herein we report our preliminary results on this subject.

Scheme 1. Metal-Free Hydrogenation of Pyridines by Boranes



We initially selected a variety of commercially available alkenes to examine the hydrogenation of 2,6-diphenylpyridine (**1a**) with H_2 (50 bar) in toluene at 100 °C for 20 h (Table 1). Piers' borane $HB(C_6F_5)_2$ itself can catalyze this reaction to give 2,6-diphenylpiperidine (**3a**) in 21% conversion (Table 1, entry 1), but the majority of boranes generated in situ by hydroboration of alkenes with $HB(C_6F_5)_2$ exhibited obviously higher activities, furnishing **3a** with excellent cis selectivity (entries 2−14). Electron-deficient alkenes were found to be more effective for this transformation (entries 7, 8, and 12), and terminal alkene **4g** gave satisfactory conversion with 98:2 dr (entry 8). Further decreasing the reaction temperature to 60 °C or the catalyst loading to 5 mol % led to a slight loss of reactivity (entries 15 and 16).

With these interesting results in hand, we next examined the substrate scope under the optimal conditions (Table 1, entry 8). As shown in Table 2, the metal-free hydrogenation of 2,6-diarylpyridines **1a−i** smoothly gave piperidines **3a−i** in 97−99% yield with 98:2 to >99:1 dr (entries 1−9). 2,6-Difurylpyridine (**1j**) was also an effective substrate, giving a

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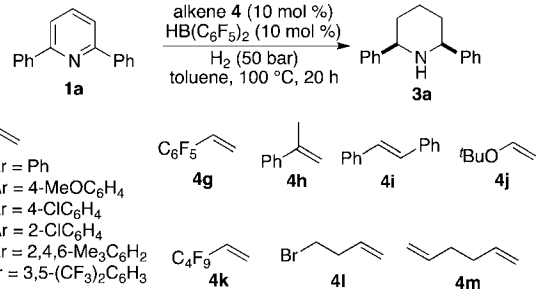
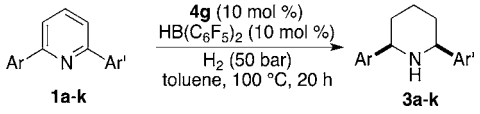
Table 1. Evaluation of Alkenes for Hydrogenation of Pyridines[a]



entry	4	conv (%)[b]	dr[b]	entry	4	conv (%)[b]	dr[b]
1[c]	–	21	nd[d]	9	**4h**	31	nd[d]
2	**4a**	59	95:5	10	**4i**	21	nd[d]
3	**4b**	72	95:5	11	**4j**	15	nd[d]
4	**4c**	62	96:4	12	**4k**	89	96:4
5	**4d**	67	96:4	13	**4l**	34	nd[d]
6	**4e**	65	96:4	14[e]	**4m**	44	nd[d]
7	**4f**	95	97:3	15[f]	**4g**	79	98:2
8	**4g**	>99	98:2	16[g]	**4g**	93	98:2

[a]All reactions were carried out with pyridine **1a** (0.25 mmol) in toluene (2.0 mL). [b]Conversion and cis:trans diastereomeric ratios were determined by ^{1}H NMR analyses of the crude reaction mixtures. [c]Without alkene. [d]Not determined. [e]5 mol % **4m**. [f]At 60 °C. [g]5 mol % catalyst.

Table 2. Hydrogenation of 2,6-Diarylpyridines[a]



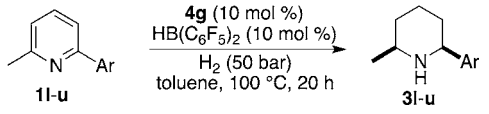
entry	product **3**	yield (%)[b]	dr[c]
1	**3a**: Ar = Ar′ = Ph	98	98:2
2	**3b**: Ar = Ar′ = 4-MeC$_6$H$_4$	97	98:2
3	**3c**: Ar = Ar′ = 4-MeOC$_6$H$_4$	99	98:2
4	**3d**: Ar = Ar′ = 4-^{t}BuC$_6$H$_4$	99	98:2
5	**3e**: Ar = Ar′ = 3-MeC$_6$H$_4$	99	98:2
6	**3f**: Ar = Ar′ = 3-MeOC$_6$H$_4$	97	98:2
7	**3g**: Ar = Ar′ = 2-MeC$_6$H$_4$	98	>99:1
8	**3h**: Ar = Ar′ = 2-MeOC$_6$H$_4$	99	>99:1
9	**3i**: Ar = Ar′ = 2-naphthyl	99	98:2
10	**3j**: Ar = Ar′ = 2-furyl	93	90:10
11	**3k**: Ar = 4-FC$_6$H$_4$, Ar′ = 4-MeOC$_6$H$_4$	92	99:1

[a]All reactions were carried out with **1** (0.25 mmol) in toluene (2.0 mL). [b]Isolated yields. [c]Determined by ^{1}H NMR analyses of the crude reaction mixtures.

high yield but exhibiting a relatively lower cis selectivity (entry 10). When pyridine **1k** containing both electron-withdrawing and electron-donating substituents was used, the desired product **3k** was obtained in 92% yield with 99:1 dr (entry 11). However, electron-deficient 2,6-bis(4-fluorophenyl)-pyridine was not a suitable substrate, giving only 23% conversion. The cis configuration of piperidines **3** was supported by the X-ray structure of piperidine **3c** (see the Supporting Information).

The series of 2-aryl-6-methylpyridines **1l–u** were also subjected to the metal-free catalytic hydrogenation. Both electron-donating and electron-withdrawing aryl substituents were well-tolerated, affording piperdines **3l–u** in 80–99% yield with excellent cis selectivity (Table 3).

Table 3. Hydrogenation of 2-Aryl-6-methylpyridines[a]



entry	product **3**	yield (%)[b]	dr[c]
1	**3l**: Ar = Ph	96	95:5
2	**3m**: Ar = 4-MeOC$_6$H$_4$	98	96:4
3	**3n**: Ar = 4-PhC$_6$H$_4$	96	96:4
4	**3o**: Ar = 4-CF$_3$C$_6$H$_4$	86	97:3
5	**3p**: Ar = 4-ClC$_6$H$_4$	88	96:4
6	**3q**: Ar = 3-MeOC$_6$H$_4$	96	96:4
7	**3r**: Ar = 3,5-Me$_2$C$_6$H$_3$	93	96:4
8	**3s**: Ar = 2-MeOC$_6$H$_4$	99	97:3
9	**3t**: Ar = 2-naphthyl	99	96:4
10	**3u**: Ar = 4-allyloxyC$_6$H$_4$	80	96:4

[a]All reactions were carried out with **1** (0.25 mmol) in toluene (2.0 mL). [b]Isolated yields. [c]Determined by ^{1}H NMR analyses of the crude reaction mixtures.

Moreover, the hydrogenation scope was further expanded to include some interesting pyridine substrates (Table 4). Reduction of the vinyl group occurred under the current reaction conditions when pyridine **1v** was used as the substrate, giving piperidine **3v** in 96% yield with 94:6 dr (entry 1). For 2-bromopyridines, an unexpected dehalogenation was observed, providing an alternative approach for the synthesis of monosubstituted piperidines (entries 2 and 7). In comparison, the direct hydrogenation of monosubstituted pyridine **1x** required a higher catalyst loading and gave a lower yield (entry 3). 2,4,6-Triaryl- and 2,6-dialkyl-substituted pyridines were hydrogenated in moderate yields (entries 4–6). Significantly, 2,2′-bipyridines proved to be effective substrates for the current catalytic system (entries 8 and 9). For 6,6′-dimethyl-2,2′-bipyridine (**1C**), one of the pyridine cycles was selectively hydrogenated to give compound **3C** as the predominant product in 59% yield, while reduction of both pyridine cycles was preferred for 6,6′-ditolyl-2,2′-bipyridine (**1D**). Moreover, under the current conditions, pyridine **1E** was hydrogenated to furnish racemic isosolenopsin A[17] in 60% yield with 93:7 dr (Scheme 2).

Our strategy for generation of borane catalysts in situ from alkenes and Piers' borane also provided the possibility of achieving the asymmetric hydrogenation of pyridines by using chiral alkenes. Several chiral dienes[15] were therefore tentatively tested for the asymmetric hydrogenation of pyridine **1C**. Unfortunately, only moderate conversion with very low enantioselectivity (<10% ee) was obtained. The asymmetric version of this transformation is still a formidable challenge and awaits further studies. Alternatively, both enantioisomers of **3C** could be easily accessed via a simple resolution process using L- or D-tartaric acid as a resolution reagent (Scheme 3). The absolute configuration was determined from the X-ray structure of crystal **1**. The interesting structures of enantiomerically pure compounds **3C** suggest their potential use as chiral organo-catalysts or ligands for asymmetric catalysis.

In summary, a broad range of pyridines have been directly hydrogenated under H_2 using catalytic amounts of simple borane catalysts generated in situ from commercially available

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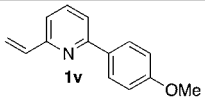
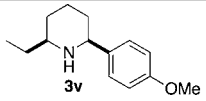
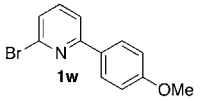
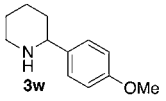
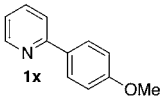
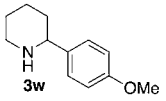
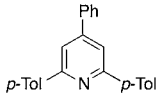
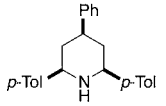
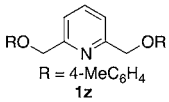
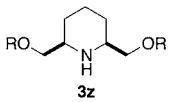
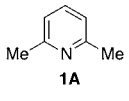
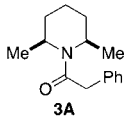
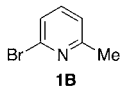
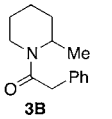
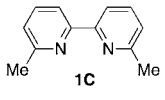
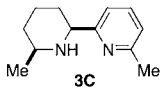
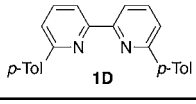
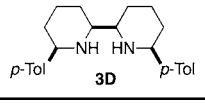
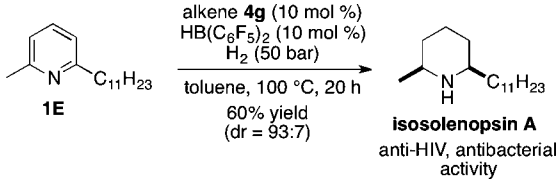
Table 4. Hydrogenation of Other Pyridines[a]

entry	pyridine **1**	product **3**	yield (%)[b,c]
1	 **1v**	 **3v**	96 (94:6)
2	 **1w**	 **3w**	80
3[d]	 **1x**	 **3w**	64
4[d]	 **1y**	 **3y**	44 (98:2)
5	 R = 4-MeC$_6$H$_4$ **1z**	 **3z**	58 (92:8)
6[e]	 **1A**	 **3A**	51
7[e]	 **1B**	 **3B**	68
8[f]	 **1C**	 **3C**	59 (96:4)
9	 **1D**	 **3D**	75 (>99:1)

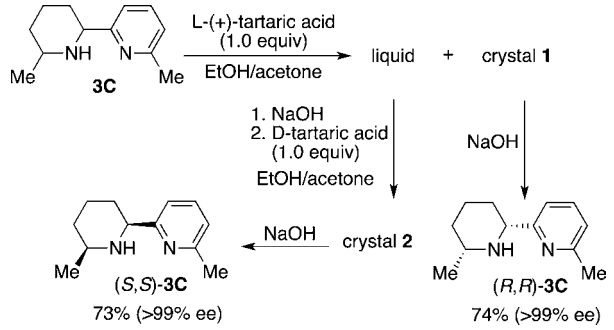
[a]All reactions were carried out with pyridine **1** (0.25 mmol), alkene **4g** (10 mol %) and HB(C_6F_5)$_2$ (10 mol %) under H_2 (50 bar) in toluene (2.0 mL) at 100 °C for 20 h, unless otherwise noted. [b]Isolated yields. [c]The dr's (in parentheses) were determined by ^{1}H NMR analyses of the crude reaction mixtures. [d]20 mol % catalyst under H_2 (75 bar) at 120 °C for 38 h. [e]The resulting piperidine was directly treated with phenylacetyl chloride and Et_3N; the reported yield is over two steps. [f]1.0 mmol of **1C** was used.

Scheme 2. Synthesis of Isosolenopsin A



alkenes and HB(C_6F_5)$_2$, furnishing important piperidines in high yields with excellent cis stereoselectivities. To the best of our knowledge, the current study represents the first successful example of metal-free catalytic hydrogenation of pyridines with H_2. Further studies to find more efficient borane catalysts,

Scheme 3. Resolution of Racemic Piperidine



expand the substrate types, and explore asymmetric transformations are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Procedures for the synthesis of pyridines, hydrogenation of pyridines, resolution of racemic piperidine; characterization of products; and crystallographic data for **3c**, **3D**, and crystal **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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