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ARTICLE TYPE

$B(C_6F_5)_3$-catalyzed metal-free hydrogenation of naphthylamines†

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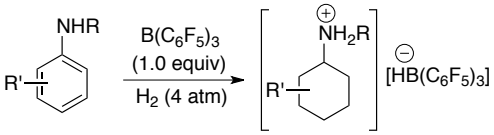
A catalytic metal-free hydrogenation of naphthylamines using $B(C_6F_5)_3$ as a catalyst was successfully achieved under mild conditions for the first time to furnish a variety of tetrahydronaphthylamines in 88-99% yields.

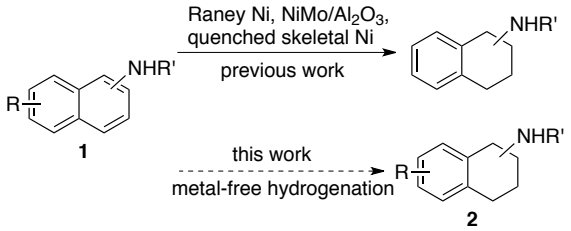
Catalytic hydrogenation of unsaturated compounds represents one of the most useful transformations in both academia and industry.[1] Particularly, the hydrogenation of hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs) to the less toxic and high-valued partial saturated materials is a very meaningful transformation for the environment and the chemical production. Usually, transition metals were the most often used catalysts for the heterogeneous or homogeneous hydrogenation of PAHs.[2,3] In contrast, the metal-free approach has been less developed. From 1989 to 1990, Köster, Yalpani, and co-workers employed boranes as catalysts to realize the hydrogenation of naphthalene, anthracene, phenanthrene and other aromatic compounds, but harsh reaction conditions were required (170-200 °C and 25-100 atm H_2).[4] The recent advent chemistry of frustrated Lewis pairs (FLPs) opens a new era for the metal-free hydrogenation.[5] A wide range of unsaturated compounds have been successfully reduced using stoichiometric or catalytic amount of FLPs.[6,7] In 2012, Stephan and Segawa reported the hydrogenation of the PAHs including anthracene derivatives, tetracene and tetraphene at 80 °C and 100 atm H_2 pressure used $B(C_6F_5)_3$ and $Ph_2PC_6F_5$ as a FLP catalyst.[8] Significantly, Stephan, Grimme, and co-workers achieved a highly challenging aromatic hydrogenation of anilines using one equivalent of $B(C_6F_5)_3$ at 110 °C and 4 atm H_2 pressure (Scheme 1).[9] Despite these advances, the development of metal-free hydrogenation of PAHs using catalytic amount of FLP catalyst under mild condition is still highly desirable.



S. Grimme and D. W. Stephan

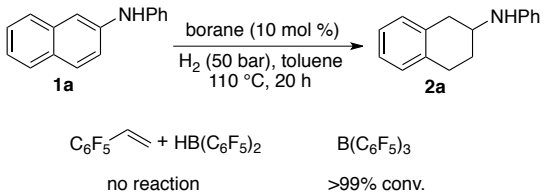
Scheme 1 Metal-free hydrogenation of anilines.

Tetrahydronaphthyl amines are important functional moieties present in various biologically active compounds.[10] The hydrogenation of naphthylamines provides a straightforward access to them. Several heterogeneous nickel catalysts have been well developed for the hydrogenation of naphthylamines **1**, and a mixture of regio-isomers was obtained in some cases (Scheme 2).[11] However, to the best of our knowledge, the metal-free homogeneous hydrogenation has rarely been reported. As part of our general interest in the FLP chemistry, recently, we reported the asymmetric hydrogenation of imines, silyl enol ethers, and 2,3-disustituted quinoxalines, and the highly *cis*-selective hydrogenation of pyridines, in which borane catalysts were generated *in situ* by the hydroboration of alkenes with Piers' borane $HB(C_6F_5)_2$.[12-14] In searching for challenging unsaturated compounds for the FLP catalysis, the hydrogenation of hazardous naphthylamines **1** to tetrahydronaphthylamines **2** attracts our interest. Herein, we wish to report our preliminary results on this subject.



Scheme 2 Catalytic hydrogenation of naphthylamines.

Initially, we examined the *in situ* catalyst generation strategy for the hydrogenation of naphthylamine **1a**. Unfortunately, in the presence of 10 mol % of Piers' borane $HB(C_6F_5)_2$ and pentafluorostyrene, the hydrogenation of naphthylamine **1a** at 110 °C with H_2 (50 bar) did not occur at all (Scheme 3), which is likely due to the relatively weaker Lewis acidity of the borane catalyst. To our pleasure, a stronger Lewis acidic borane $B(C_6F_5)_3$[15] can give a quantitative conversion under the same conditions, and the reduction of the phenyl ring in naphthylamine **1a** was not observed(Scheme 3).



Scheme 3 Metal-free hydrogenation of naphthylamine **1a**.

The reaction conditions were further optimized, and some results are summarized in Table 1. The $B(C_6F_5)_3$-catalyzed hydrogenation of naphthylamine **1a** went smoothly at 60 °C with

H_2 (20 bar) for 6 h to give tetrahydronaphthylamine **2a** in a quantitative conversion (Table 1, entry 5). Further reducing the catalyst loading from 10 mol % to 5 mol % only led a slight lower conversion (Table 1, entry 6). Solvents were found to have an obvious influence on the reactivities, and toluene proved to be the optimal solvent (Table 1, entries 5, 7-10).

Table 1 Optimization of reaction conditions for hydrogenation of naphthylamine **1a**[a]

Entry	Catalyst (mol %)	H_2 (bar)	Solvent	Temp. (°C)	Time (h)	Conv. (%)[b]
1	10	50	Toluene	110	20	>99
2	10	50	Toluene	110	6	>99
3	10	50	Toluene	60	6	>99
4	10	50	Toluene	rt	20	92
5	**10**	**20**	**Toluene**	**60**	**6**	**>99**
6	5	20	Toluene	60	6	95
7	10	20	Hexane	60	6	97
8	10	20	CH_2Cl_2	60	6	98
9	10	20	C_6H_5Br	60	6	78
10	10	20	Et_2O	60	6	58

[a] All reactions were carried out with naphthylamine **1a** (0.25 mmol) in solvent (2.0 mL). [b] Determined by crude ^{1}H NMR.

The substrate scope for the metal-free hydrogenation was next studied under the optimal conditions. As shown in Table 2, several aryl-protecting groups for 2-naphthylamines were well tolerated for this transformation to give the desired products **2a-f** in 90-99% yields (entries 1-6). But free 2-naphthylamine and 2-nathphtylamines bearing alkyl-protecting groups (Bn or *tert*-butyl) were not suitable substrates for this reaction. Various substituents at the 6 or 7-position of 2-naphthylamines gave high yields, except that a longer reaction time was required for the electron-withdrawing substituents (Table 2, entries 7-10). Naphthyldiamines were also effective substrates for the hydrogenation to give products **2k** and **2l** in high yields (Table 2, entries 11 and 12). The hydrogenation of *N*-phenyl-2-anthracene proceeded well to afford the desired product **2m** in 95% yield (Table 2, entry 13). Moreover, 1-naphthylamines were also suitable substrates for the metal-free hydrogenation to furnish tetrahedronaphthyl amines **2n-p** in 92-95% yields (Table 2, entries 14-16). However, the introduction of additional substituents to the aromatic ring containing the amine groups will inhibit the hydrogenation (Figure 1). Further efforts on searching for more efficient catalysts are still necessary to solve this restriction.

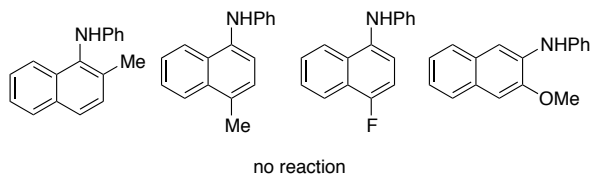


Figure 1 Unreactive substrates for the hydrogenation.

Conclusions

In summary, the first metal-free hydrogenation of naphthylamines was successfully achieved using 10 mol % of $B(C_6F_5)_3$ as a catalyst under a mild condition, and a variety of

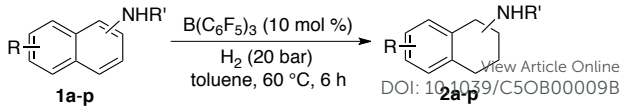
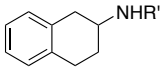
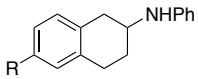
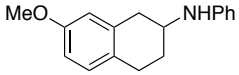
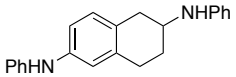
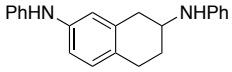
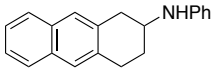
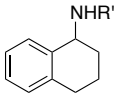
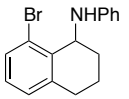


Table 2. Metal-free hydrogenation of naphthylamines **1**[a]

Entry	Product (**2**)	Yield (%)[b]
		
1	**2a**: R' = Ph	94
2	**2b**: R' = 4-MeC_6H_4	95
3	**2c**: R' = 4-MeOC_6H_4	90
4	**2d**: R' = 4-ClC_6H_4	98
5	**2e**: R' = 4-FC_6H_4	99
6	**2f**: R' = 2,4,6-$Me_3C_6H_2$	93
		
7	**2g**: R = OMe	91
8[c]	**2h**: R = CO_2Me	90
9[c]	**2i**: R = F	95
		
10	**2j**	89
		
11	**2k**	88
		
12[d]	**2l**	93
		
13	**2m**	95
		
14	**2n**: R' = Ph	94
15	**2o**: R' = 4-MeC_6H_4	95
		
16	**2p**	92

[a] All reactions were carried out with naphthylamines **1** (0.25 mmol) and $B(C_6F_5)_3$ (0.025 mmol) in toluene (2.0 mL) under H_2 (20 bar) at 60 °C for 6 h unless otherwise noted. [b] Isolated yield. [c] Reaction time was 20 h. [d] The reaction was run at 45 °C for 20 h.

tetrahydronaphthylamines were furnished in 88-99% yields. This mild condition provides a possibility for the development of asymmetric reactions by searching for effective chiral borane catalysts. Further efforts on expanding the substrate scope and developing the asymmetric transformation are underway in our laboratory.

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Notes and references

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