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Hydrogenation of olefins using Hantzsch ester catalyzed by palladium on carbon

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ABSTRACT

Hantzsch 1,4-dihydropyridine (HEH), a well-known model compound of coenzyme NAD(P)H was found as an efficient reducing agent in hydrogenation of unactivated olefins catalyzed by Pd/C. α,β -Unsaturated ketones also underwent hydrogenation, affording the corresponding saturated ketones selectively.

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It is well known that Pd/C is a cost-efficient heterogeneous catalyst and is used extensively in organic chemistry.¹ Some dehydrogenation reactions using Pd/C catalyst have been reported but the yields were not satisfactory. Recently, Hayashi and his co-workers developed an efficient dehydrogenation reaction using Pd/C under an ethylene atmosphere.² In the Pd/C-ethylene system, ethylene played a crucial role and it was used to remove hydrogen from the active surface of catalyst. Pd/C has also been employed to catalyze dehydrogenative aromatizations of hydroaromatic compounds. For instance, a Pd/C-acetic acid system was successfully applied to the oxidation of Hantzsch 1,4-dihydropyridines (HEHs) to pyridines.³ HEH is being investigated as a safe, easy-to-handle, cheap, and environmentally benign reagent for the reduction of organic functional groups.⁴ In continuing our efforts to develop HEH-based synthetic methods,⁵ we began to wonder whether hydrogen which is produced by dehydrogenative aromatizations of HEH in the presence of Pd/C could be efficiently accepted by olefins.

Many studies have been conducted concerning the mechanism of HEH's reduction of various electron-deficient functional groups.^{4a,6} Recently, there has been much interest in finding an application for HEH as a biomimetic reducing agent in organo-catalytic and enantioselective reduction of α,β -unsaturated aldehydes,⁷ α,β -unsaturated ketones,⁸ and nitroolefins.⁹ To our knowledge, there is still no report on hydrogenation of unacti-

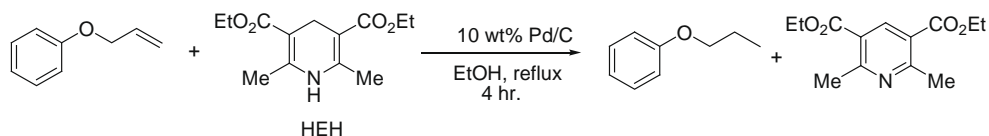
vated olefins with HEH. Herein, we reported the results of our research.

It had been reported that ethylene was not hydrogenated to ethane in oxidative aromatization process to convert 1,4-dihydropyridines to the corresponding pyridines by using a catalytic amount of Pd/C in acetic acid.³ Hence, various solvents such as CH₃CN, THF, PhCH₃, ClCH₂CH₂Cl, and EtOH were screened for the hydrogenation of olefins, and the best results were observed under ethanol conditions. Typical procedure is as follows: an ethanolic solution (20 mL) of allyloxybenzene (1.0 mmol), HEH (1.1 mmol), and 10% Pd/C (10 wt % of allyloxybenzene) was refluxed under stirring and argon atmosphere for 4 h. After completion of the reaction as monitored by TLC, the solvent was filtered and the filtrate was concentrated under reduced pressure. The corresponding saturated propoxybenzene was isolated in 86% yield by a column chromatography (silica gel). Besides propoxybenzene, diethyl 2,6-dimethyl-3,5-pyridinedicarboxylate, the corresponding oxidative aromatizing product of HEH, was also isolated (Scheme 1). All products were identified by comparing its ¹H NMR, ¹³C NMR, and EI-MS spectral data.

With this initial success, the scope of this protocol was examined for other substrates. Typical results are summarized in Table 1. It is seen from Table 1 that the present procedure affords a very clean and efficient approach for hydrogenation of aliphatic and aromatic olefins. Both terminal olefins (entries 1, 3, 4, and 5) and internal olefins (entries 2, 6, and 7) afforded the saturated products in an excellent yield. The hydrogenation of indene also proceeded smoothly giving indan in 89% yield (entry 8).

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Scheme 1.

Table 1
Pd/C-catalyzed hydrogenation of olefins with HEH^a

Entry	Substrate	Product	Yield ^b (%)
1			88
2			89
3			90
4			90
5			99
6			99
7			99
8			90

^a Reaction conditions see text.

^b Isolated yields. All products are known compounds and were characterized by EI-MS, ¹H NMR, and ¹³C NMR.

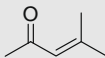
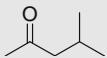
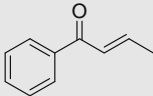
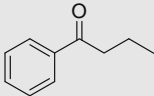
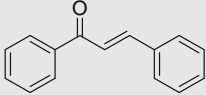
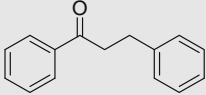
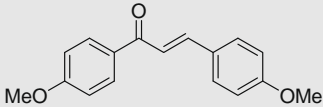
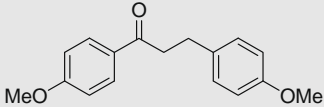
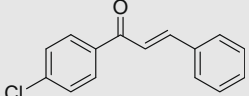
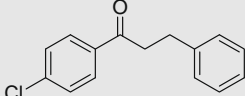
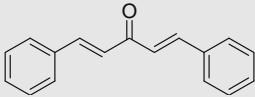
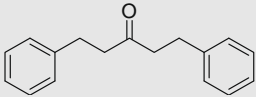
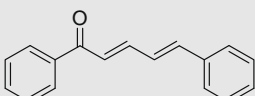
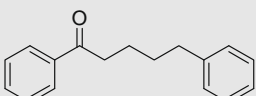
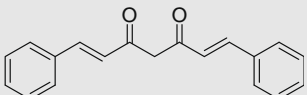
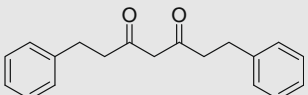
α,β -Unsaturated ketones also underwent the present hydrogenation, although a relatively more amount of Pd/C (20 wt % of substrates) and a longer reaction time (8 h) were needed to complete the reaction. In these cases, 1,4-reduced products were obtained selectively and no alcohol product was observed. Typical results are summarized in Table 2. The procedure worked well on aliphatic 2-en-1-one (entry 1), phenyl aliphatic 2-en-1-one (entry 2), and chalcone analogs (entries 3–5). The method was also successfully extended to 1,4-dien-3-one (entry 6), 2,4-dien-1-one (entry 7), and 1,6-diene-3,5-dione (entry 8) systems. In the present case, all double bonds were reduced by using 2.1 equiv of HEH and the corresponding saturated ketones were isolated as the major products.

The comparison of the present method with H₂ hydrogenation under ordinary pressure in the presence of 10% Pd/C at room temperature was also carried out. It seems that both methods worked

well with unactivated olefins. But the advantage of HEH-based hydrogenation was shown significantly in hydrogenation of α,β -Unsaturated ketones. For instance, the Pd/C-catalyzed hydrogenation of chalcone with molecular hydrogen resulted in a mixture of 1,3-diphenylpropan-1-one (73%) and 1,3-diphenylpropan-1-ol (21%) even in 15 min, while the present method gave 1,3-diphenylpropan-1-one in 96% yield.

In summary, the Pd/C-catalyzed hydrogenation of olefins with HEH is described. Although the catalyzed reduction of electron-deficient olefins with HEH has been well studied,^{6–9} there is no report on hydrogenation of unactivated alkenes with HEH. The present reaction expands the application of HEH as a biomimetic reducing agent in synthetically useful organic transformations, and provides a simple and easy way for the hydrogenation of olefins without expensive reagents and pressurized conditions.

Table 2
Selective reduction of α,β -unsaturated ketones by HEH in the presence of Pd/C^a

Entry	Substrate	Product	Yield ^b (%)
1			93 ^c
2			89
3			96
4			96
5			81
6			93 ^d
7			88 ^d
8			90 ^d

^a The reaction was carried out in refluxing ethanol (25 mL) for 8 h using α,β -unsaturated ketones (1.0 mmol), HEH (1.1 mmol) in the presence of 10% Pd/C (20 wt % of corresponding α,β -unsaturated ketones).

^b Isolated yields. All products are known compounds and were characterized by EI-MS, ¹H NMR, and ¹³C NMR.

^c The yield was determined by GC-MS.

^d 2.1 Equiv of HEH was needed to complete the reactions.

Acknowledgments

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