



Dehydrogenation of 1,2,3,4-tetrahydroquinoline and its related compounds: comparison of Pd/C–ethylene system and activated carbon–O₂ system

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ABSTRACT

Dehydrogenation of substituted 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline, and 1,2,3,4-tetrahydrocarbazole proceeded using Pd/C–ethylene system (method A) or activated carbon–O₂ system (method B) to give the corresponding heteroaromatic compounds.

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We previously reported the oxidation method of benzylic and allylic alcohols using Pd/C–ethylene system.¹ After that, we found some kinds of activated carbons themselves promoted the oxidation including oxidative aromatization, carbonylation, and oxidation of benzylic alcohols.² In the course of the above study, we briefly mentioned dehydrogenation of 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline, and 1,2,3,4-tetrahydrocarbazole proceeded using Pd/C–ethylene system to afford the corresponding heteroaromatic compounds in 2002.³ Recently, Luo and Crabtree reported dehydrogenation reaction of nitrogen- and oxygen-containing heterocycles in 2006.⁴ Furthermore, there have been some reports on dehydrogenative oxidation of amines using transition metal such as Cp^{*}Ir complex,⁵ Cu-salene complex,⁶ Co₃O₄-supported hydrous RuO₂,⁷ supported ruthenium hydroxide catalysis (Ru(OH)_x/Al₂O₃),⁸ and dirhodium caprolactamate.⁹ Here, we reported that dehydrogenation of 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline, and 1,2,3,4-tetrahydrocarbazole proceeded using Pd/C–ethylene system (method A). Furthermore, we have revealed that only activated carbon promotes this reaction in the presence of oxygen (method B) (Scheme 1). As for oxidative conversion of 1,2,3,4-tetrahydroquinoline (**1**) to quinoline (**7**), Pratt and McGovern reported the method using 8 equiv of MnO₂ in benzene at 81 °C to give **7** in 79% yield.¹⁰ Concerning oxidative conversion of the compound **5**, Wolthuis reported the method using 50 wt % of 5% Pd/C in mesitylene at reflux temperature (bp 162–164 °C) to give **11** in 72% yield.¹¹

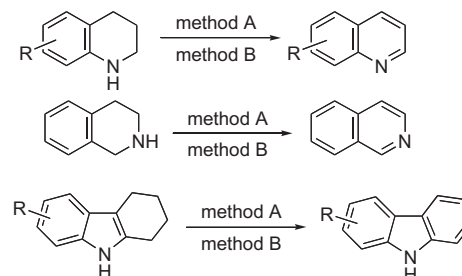
Pd/C–ethylene system (method A): When 1,2,3,4-tetrahydroquinolines (**1**, **2**, and **3**), 1,2,3,4-tetrahydroisoquinoline (**4**), and 1,2,3,4-tetrahydrocarbazoles (**5** and **6**) were treated with 50 wt % of 10% Pd/C in acetonitrile under ethylene atmosphere, the corre-

sponding hetero aromatic compounds (**7–12**), that is, quinolines, isoquinolines, and carbazoles were obtained in high yield (Table 1).

We suggested that method A included hydrogen transfer reaction. To confirm this, in the Pd/C–ethylene system, we actually detected the generation of ethane by GC analysis (Hewlett-Packard 5890 series II, Porapak R column: 40 °C: retention time (*t_R*) of ethylene, 2.3 min; *t_R* of ethane, 3.3 min) (Scheme 2). Excess amount of ethylene was also observed.

It should be mentioned that in the presence of ethylene, the product was only heteroaromatic compound, whereas, in the absence of ethylene, the reaction gave some by-products. These results will be consistent with the above results, that is, ethylene is smoothly hydrogenated to ethane, therefore, we judge that method A involves hydrogenation transfer reaction.

Activated carbon–O₂ system (method B): We found that the conversion of 1,2,3,4-tetrahydroquinolines (**1**, **2**, and **3**), 1,2,3,4-tetra-



method A: Pd/C–ethylene, method B: activated carbon–O₂

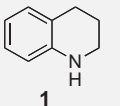
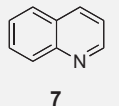
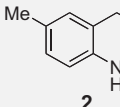
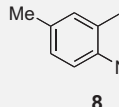
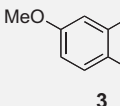
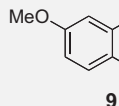
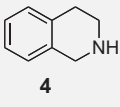
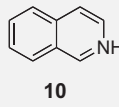
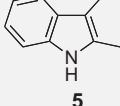
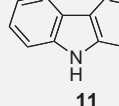
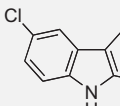
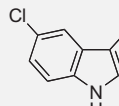
Scheme 1. Dehydrogenation of nitrogen-containing 1,2,3,4-tetrahydroaromatic compounds using Pd/C–ethylene system (method A) or activated carbon–O₂ system (method B).

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Table 1

Oxidation of 1,2,3,4-tetrahydroquinolines (**1**, **2**, and **3**), 1,2,3,4-tetrahydroisoquinoline (**4**), and 1,2,3,4-tetrahydrocarbazoles (**5** and **6**) using Pd/C–ethylene system (method A) and activated carbon–O₂ system (method B).

Entry	Substrate	Product	Yield ^a (%)	
			Method A ^b	Method B ^c
1			75	86
2			40	86
3			39	87
4			50	75 ^d
5			92 ^e	77
6			69 ^e	53 ^e

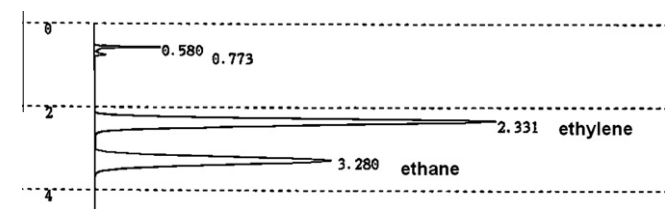
^a Isolated yield by silica gel column chromatography unless otherwise noted.

^b Method A: Pd/C–ethylene, in CH₃CN, 50 wt % of 10% Pd/C, 100 °C, 96 h.

^c Method B: activated carbon, in xylene, 100 wt % activated carbon, 120 °C, 24 h.

^d 96 h.

^e Isolated yield by recrystallization.



Scheme 2. Detection of the generation of ethane using Pd/C–ethylene system.

hydroisoquinoline (**4**), and 1,2,3,4-tetrahydrocarbazoles (**5** and **6**) to the corresponding heteroaromatic compounds also proceeded by the aid of only activated carbon under the oxygen atmosphere. The results are summarized in Table 1. As for the role of activated carbon as a promoter, after examining the effects on reactivity in the oxidative aromatization, we found that the essential role of activated carbon in this oxidation system is concerned not only with specific surface area, pore volume, mean pore diameter and surface oxygen groups evolving as CO₂ at 900 °C but also with surface oxygen groups evolving as CO during heating at 900 °C, such as carbonyl groups on the surface of activated carbon.

This reaction would involve dehydration (not dehydrogenation) via radical species. It should be noted that in the absence of activated carbon the reaction of tetrahydroquinoline **1** did not take place even under O₂ atmosphere at 120 °C for 24 h.

In summary, dehydrogenation of substituted 1,2,3,4-tetrahydroquinoline (**1**, **2**, and **3**), 1,2,3,4-tetrahydroisoquinoline (**4**), and 1,2,3,4-tetrahydrocarbazoles (**5** and **6**) proceeded using Pd/C–ethylene system (method A) or activated carbon–O₂ system (method B) to give the corresponding heteroaromatic compounds. When we compared method A with method B, for the oxidation of 1,2,3,4-tetrahydroquinolines (**1**, **2**, and **3**) and 1,2,3,4-tetrahydroisoquinoline (**4**), method B was found to be superior in the point of reactivity. On the other hand, for 1,2,3,4-tetrahydrocarbazoles (**5** and **6**), method A afforded higher yield compared with method B.^{12–16}

Acknowledgments

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- Typical procedure for the oxidation of tetrahydroheteroaromatic compounds to heteroaromatic compounds by activated Pd/C–ethylene system: Synthesis of quinoline (7).* A dry Schlenk tube containing stirring bar under an ethylene atmosphere was charged with 1,2,3,4-tetrahydroquinoline (266.4 mg, 2 mmol) and acetonitrile (1.5 mL). To this mixture was added 50 wt % of 10% Pd/C and the mixture was stirred vigorously at 100 °C for 96 h under ethylene atmosphere using a balloon. After confirmation of the completion of the reaction by TLC, the palladium precipitate was filtered off. After removal of the solvent, the product was purified by silica gel column chromatography to give quinoline in 194.1 mg (75%). All spectral data of the products were identical with those of commercially available authentic samples. *R*_f = 0.59 (hexane/ethyl acetate = 1:2); IR (KBr): ν_{\max} (cm⁻¹) 3056, 3036, 1932, 1620, 1596, 1529, 1570, 1501, 1313, 1118, 939, 805, 611; ¹H NMR (400 MHz, CDCl₃): δ 8.92 (d, *J* = 4.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.40 (dd, *J* = 4.4, 4.4 Hz, 1H).
- Typical procedure for the oxidation of 1,2,3,4-tetrahydroquinoline to quinoline by activated carbon–O₂ system: Synthesis of quinoline (7).* A mixture of 1,2,3,4-tetrahydroquinoline (133.2 mg, 1 mmol), 100 wt % of activated carbon (Charcoal Activated, TOKYO CHEMICAL INDUSTRY CO., LTD (TCI)), and anhydrous xylene (5 mL) was placed in a three-necked flask under an oxygen atmosphere using a balloon. The whole was heated to 120 °C and stirred for 24 h at this temperature. After confirmation of the completion of the reaction by TLC analysis (hexane/ethyl acetate = 1:2), activated carbon was filtered off using Celite. After washing with ethyl acetate, the filtrate was evaporated and the resulting liquid was purified by silica gel column chromatography. Quinoline was obtained in 111.1 mg (86% yield).
- Synthesis of isoquinoline (10).* A mixture of various 1,2,3,4-tetrahydroisoquinoline (133 mg, 1 mmol), 100 wt % of activated carbon (Charcoal Activated, TOKYO CHEMICAL INDUSTRY CO., LTD (TCI)), and anhydrous xylene (5 mL) was placed in a three-necked flask under an oxygen atmosphere using a balloon. The whole was heated to 120 °C and stirred for 96 h at this temperature. After confirmation of the completion of the reaction by TLC analysis (hexane/ethyl acetate = 1:2), activated carbon was filtered off using Celite. After washing with ethyl acetate, the filtrate was evaporated and the resulting liquid was purified by silica gel column chromatography. Isoquinoline was obtained in 96.9 mg (75% yield). *R*_f = 0.4 (hexane/ethyl acetate = 1:2); IR (KBr): ν_{\max} (cm⁻¹) 3402, 3056, 1924, 1627, 1588, 1498, 1382, 1273, 1141, 1014, 944, 862, 827, 742, 638; ¹H NMR (400 MHz, CDCl₃): δ 9.20 (s, 1H), 8.52 (d, *J* = 6.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.7–7.6 (m, 3H).
- Synthesis of carbazole (11).* A mixture of various 1,2,3,4-tetrahydrocarbazole (171 mg, 1 mmol), 100 wt % of activated carbon (Charcoal Activated, TOKYO CHEMICAL INDUSTRY CO., LTD (TCI)), and anhydrous xylene (5 mL) was placed

in a three-necked flask under an oxygen atmosphere using a balloon. The whole was heated to 120 °C and stirred for 24 h at this temperature. After confirmation of the completion of the reaction by TLC analysis (hexane/ethyl acetate = 2:1), activated carbon was filtered off using Celite. After washing with ethyl acetate, the filtrate was evaporated and the resulting solid was purified by silica gel column chromatography. Carbazole was obtained in 128.8 mg (77%). $R_f = 0.62$ (hexane/ethyl acetate = 2:1); mp 244–246 °C (lit.¹⁷ 243.5–246 °C); IR (KBr): ν_{\max} (cm⁻¹) 3418, 3049, 2924, 1601, 1494, 1451,

1327, 1237, 928, 748, 725; ¹H NMR (400 MHz, CDCl₃): δ 11.3 (br s, 1H), 8.10 (d, $J = 7.6$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.15 (t, $J = 7.6$ Hz, 1H).

16. For all other products, IR and ¹H NMR spectra were identified with authentic compounds.
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