

# Hydrogen Self-Sufficient Arene Reduction to Cyclohexane Derivatives Using a Combination of Platinum on Carbon and 2-Propanol

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Received: March 16, 2015; Revised: July 1, 2015; Published online: September 25, 2015

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201500263>.

**Abstract:** Various arenes have been hydrogenated using platinum on carbon in a 2-propanol-aqueous mixed solvent at 100 °C without the addition of flammable hydrogen gas to give the corresponding cyclohexane derivatives. 2-Propanol plays a role as an efficient hydrogen source based on the platinum on carbon-catalyzed dehydrogenation.

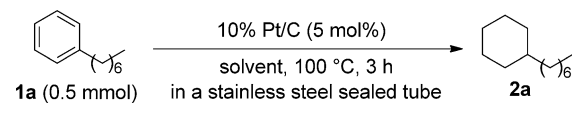
**Keywords:** arene reduction; dehydrogenation; hydrogen self-sufficiency; platinum on carbon; 2-propanol

The reduction of arenes<sup>[1-5]</sup> is an important and straightforward method to provide cyclohexane derivatives, which can be storage materials of hydrogen gas in the energy field<sup>[6]</sup> and precursors to construct functional materials. Additionally, the arene reduction is also used to remove aromatic compounds from fuel since they cause a decrease in the combustion efficiency.<sup>[2]</sup> Although arene hydrogenation using heterogeneous catalysts is regarded as an efficient method from the viewpoint of green chemistry due to the easy removal of the catalyst from the reaction mixture,<sup>[2b,3,4]</sup> the excess use of flammable hydrogen, which is required to be strictly administered in a gas cylinder and safety cabinet, is still a problematic issue. Although only one example using *in situ*-generated hydrogen derived from Al powder and H<sub>2</sub>O in the presence of heterogeneous transition metal catalysts was reported, a large amount of Al sludge was produced as a by-product.<sup>[5]</sup> We have also reported the Rh/C- or Ru/C-catalyzed hydrogenation of arenes<sup>[4]</sup> and recently developed a platinum group metal on carbon (e.g., Pt/C and Rh/C)-catalyzed dehydrogenation of alcohols [2-propanol (*i*-PrOH), etc.] to give the corre-

sponding carbonyl products and molecular hydrogen, which was utilized in hydrogenation and deuteration reactions.<sup>[7]</sup> We now report an efficient Pt/C-catalyzed and hydrogen self-sufficient arene reduction in an *i*-PrOH/H<sub>2</sub>O mixed solvent based on the Pt/C-catalyzed dehydrogenation of *i*-PrOH.

First, the solvent effect was investigated using heptylbenzene (**1a**; 0.5 mmol) as a substrate in the presence of 10% Pt/C (5 mol%) at 100 °C for 3 h in a stainless steel sealed tube as a reaction vessel (Table 1). While the single application of *i*-PrOH as a solvent was also effective for the production of the desired cyclohexane derivative (**2a**) (entry 1), the addition of H<sub>2</sub>O as a co-solvent further improved the reaction efficiency to give **2a** as the sole product in 97%

**Table 1.** Solvent effect in Pt/C-catalyzed reduction of *n*-heptylbenzene (**1a**) in a stainless steel sealed tube.



Entry	Solvent	Ratio of <b>1a</b> / <b>2a</b> <sup>[a]</sup>
1	<i>i</i> -PrOH (6 mL)	18/82
2	<i>i</i> -PrOH (4 mL)/H <sub>2</sub> O (2 mL)	0/100 (97%) <sup>[b]</sup>
3 <sup>[c]</sup>	<i>i</i> -PrOH (4 mL)/H <sub>2</sub> O (2 mL)	63/37
4 <sup>[d]</sup>	<i>i</i> -PrOH (4 mL)/H <sub>2</sub> O (2 mL)	4/96
5	MeOH (4 mL)/H <sub>2</sub> O (2 mL)	100/0
6	<i>t</i> -BuOH (4 mL)/H <sub>2</sub> O (2 mL)	100/0
7	H <sub>2</sub> O (6 mL)	100/0
8	<i>i</i> -PrOH (4 mL)/THF (2 mL)	100/0
9	<i>i</i> -PrOH (4 mL)/cyclohexane (2 mL)	70/30
10	<i>i</i> -PrOH (4 mL)/CH <sub>2</sub> Cl <sub>2</sub> (2 mL)	100/0

<sup>[a]</sup> The ratio was determined by <sup>1</sup>H NMR.

<sup>[b]</sup> Isolated yield.

<sup>[c]</sup> At 80 °C.

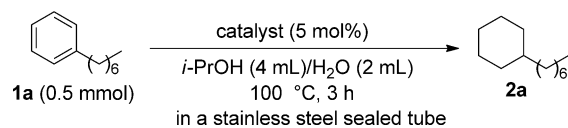
<sup>[d]</sup> At 120 °C.

isolated yield (entry 2).<sup>[8]</sup> On the other hand, the reaction in MeOH/H<sub>2</sub>O, *t*-BuOH/H<sub>2</sub>O or H<sub>2</sub>O never proceeded, and THF, cyclohexane and CH<sub>2</sub>Cl<sub>2</sub> were inefficient co-solvents of *i*-PrOH (entries 5–10). The optimal reaction temperature (100 °C) became evident in comparison to the reactions at 80 and 120 °C (entries 2 vs. 3 and 4).

10% Pt/C very smoothly catalyzed the reduction of **1a**, while the use of 5% Pt/Al<sub>2</sub>O<sub>3</sub> caused a delay in the reduction (Table 2, entries 1 vs. 5). PtO<sub>2</sub>, 10% Pd/C and 10% Rh/C indicated no catalytic activity (entries 6–8), and the 10% Ru/C- or 10% Ir/C-catalyzed reduction was never completed even after 3 h reaction time (entries 9 and 10). While the arene reduction could proceed by the use of 5% Pt/C purchased from either commercial supplier, 5% Pt/C supplied from N. E. Chemcat Corporation (AC-1501) was most active (entries 2–4). Furthermore, 10% Pt/C could be reused without a decrease in the catalyst activity (entry 11) and the scale-up using 2.5 mmol of **1a** was accomplished.

The optimized reaction conditions using 10% Pt/C in *i*-PrOH/H<sub>2</sub>O at 100 °C were applied to the reduction of various arene substrates (Table 3). *N*-Methyl-

**Table 2.** Catalyst efficiency.



Entry	Catalyst	Ratio of <b>1a/2a</b> <sup>[a]</sup>
1 <sup>[b]</sup>	10% Pt/C	0/100 (97%) <sup>[c]</sup>
2 <sup>[b]</sup>	5% Pt/C	0/100
3 <sup>[c]</sup>	5% Pt/C	33/67
4 <sup>[d]</sup>	5% Pt/C	82/18
5	5% Pt/Al <sub>2</sub> O <sub>3</sub>	66/34
6	PtO <sub>2</sub>	100/0
7 <sup>[b]</sup>	10% Pd/C	100/0
8 <sup>[b]</sup>	10% Rh/C	100/0
9 <sup>[b]</sup>	10% Ru/C	45/55
10 <sup>[b]</sup>	10% Ir/C	24/76
11 <sup>[b,f]</sup>	10% Pt/C	0/100 (94%) <sup>[c]</sup>
12 <sup>[b,g]</sup>	10% Pt/C	0/100 (91%) <sup>[c]</sup>

<sup>[a]</sup> The ratio was determined by <sup>1</sup>H NMR.

<sup>[b]</sup> Catalysts are obtainable from N. E. Chemcat Corporation (AC-1501).

<sup>[c]</sup> Catalyst was purchased from Wako Pure Chemical Industries, Ltd. (167-13911).

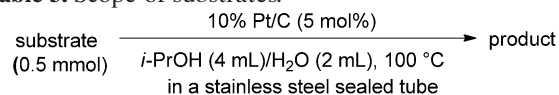
<sup>[d]</sup> Catalyst was purchased from Sigma–Aldrich Co. (20,593-1).

<sup>[e]</sup> Isolated yield.

<sup>[f]</sup> 10% Pt/C recovered after the reaction of entry 1 was reused.

<sup>[g]</sup> The reaction was carried out using **1a** (2.5 mmol) in 10 mL of *i*-PrOH and 5 mL of H<sub>2</sub>O in a 50-mL stainless steel sealed tube for 6 h.

**Table 3.** Scope of substrates.



Entry	Substrate	Product	Yield <sup>[a]</sup> (Time)
1	<b>1b</b>	<b>2b</b>	97% (48 h)
2	<b>1c</b>	<b>2c</b>	96% (4 h)
3	<b>1d</b>	<b>2d</b>	85% (48 h)
4	<b>1e</b>	<b>2e</b>	94% (24 h)
5	<b>1f</b>	<b>2f</b>	97% (12 h)
6 <sup>[b]</sup>	<b>1g</b>	<b>2g</b>	92% (24 h)
7	<b>1h</b>	<b>2h</b>	86% (48 h) [ <i>cis:trans</i> = 62:38]
8	<b>1i</b>	<b>2i</b>	83% (48 h)
9	<b>1j</b>	<b>2j</b>	97% (24 h)
10	<b>1k</b>	<b>2k</b>	95% (24 h)
11	<b>1l</b>	<b>2f</b>	91% (36 h)

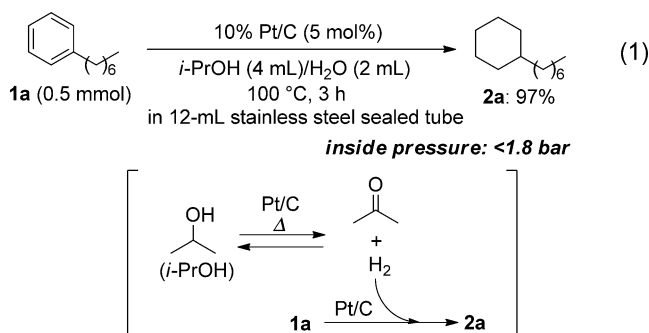
<sup>[a]</sup> Isolated yield.

<sup>[b]</sup> 10 mol% of 10% Pt/C was used.

benzamide (**1b**), acetanilide (**1c**) and benzoic acid (**1d**) underwent the reduction of only the corresponding arene nuclei to give cyclohexane derivatives (**2b–d**) in good yields (entries 1–3). Biphenyl (**1e**) and biphenylmethane (**1f**) possessing two aromatic nuclei within the molecule were also efficiently transformed into cyclohexyl compounds (**2e** and **f**), and the reduction of fluorene (**1g**) and naphthalene (**1h**) gave tricyclic and bicyclic products (**2g** and **h**), respectively (entries 4–7). Meanwhile, anthracene (**1i**) was partially hydrogenated and only the central aromatic nucleus remained as a 1,2,4,5-tetrasubstituted benzene deriva-

tive (entry 8). Furthermore, the coexisting reducible functionalities, such as the alkene and benzylic alcohol functionalities of cinnamic acid (**1j**), stilbene (**1k**) and benzhydrol (**1l**), were completely hydrogenated to give the corresponding saturated cyclohexane derivatives (entries 9–11).

During the reduction of **1a**, the inside pressure in the stainless steel sealed tube slightly increased up to 1.8 bar regardless of the distention of the enclosed gas by heat [Eq. (1)].<sup>[9]</sup> Therefore, the Pt/C-catalyzed hydrogen generation by the dehydrogenation of *i*-PrOH proceeded quite gently and the resulting hydrogen was smoothly consumed by the reduction of the arene with the formation of acetone. Since the excess hydrogen facilitates the Pt/C-catalyzed hydrogenation of acetone (the reverse reaction of dehydrogenation of *i*-PrOH), the total amount of the generated flammable hydrogen is restricted.



In conclusion, we have established the Pt/C-catalyzed and hydrogen self-sufficient hydrogenation of arenes in a isopropyl alcohol-aqueous mixed solvent to give the corresponding cyclohexane derivatives. *i*-PrOH can be a gentle hydrogen source based on the Pt/C-catalyzed dehydrogenation, and the present method restricted the excess generation of flammable hydrogen. Therefore, the present safe and mild methodology is expected to find use for the syntheses of various cyclohexane derivatives.

## Experimental Section

### General Procedure

A suspension of an arene (0.5 mmol), 10% Pt/C (5 mol%) in *i*-PrOH (4 mL) and H<sub>2</sub>O (2 mL) in a 12-mL stainless steel sealed tube was stirred at 100 °C. After stirring for a specific reaction time, the mixture was cooled to room temperature and filtered using a membrane filter (Milipore, Millex<sup>®</sup>-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with Et<sub>2</sub>O (20 mL) and H<sub>2</sub>O (20 mL), and then the aqueous layer was further extracted with Et<sub>2</sub>O (10 mL × 3). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, fil-

tered and concentrated under vacuum to give the analytically pure cyclohexane product.

## Acknowledgements

This work was partially supported by the Research Foundation for Pharmaceutical Sciences for Y. S. and the Sasakawa Scientific Research Grant for T. Y. Furthermore, we thank the N. E. Chemcat Corporation for the kind gift of 10% Pt/C.

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- [8] Although the effect of H<sub>2</sub>O is unclear, the platinum group metal on carbon-catalyzed dehydrogenation was effectively promoted in the presence of H<sub>2</sub>O. See ref.<sup>[7]</sup>
- [9] The inside pressure of the stainless steel sealed tube in the presence of **1a** and *i*-PrOH (4 mL)/H<sub>2</sub>O (2 mL) without 10% Pt/C (no hydrogen gas and reduction of **1a**) increased to 1.2 bar at 100°C. Therefore, a slight amount of hydrogen accumulated in the stainless steel sealed tube under the Pt/C-catalyzed reaction conditions shown in Eq. (1).
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