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Hydrogenation of olefins using water and zinc metal catalyzed by a rhodium complex

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Abstract—The hydrogenation of olefins using H_2O or D_2O as a hydrogen source and zinc metal as a reducing agent has been found to be catalyzed by a rhodium complex. α,β-Unsaturated ketones also underwent hydrogenation, affording the corresponding saturated ketones selectively.
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Transition-metal-catalyzed hydrogenation of carbon–carbon multiple bonds is one of the most important reactions in synthetic and industrial chemistry.[1] Hydrogen gas is usually used in hydrogenation reactions;[1] however, it requires the handling of a highly flammable hydrogen gas and pressurized conditions. Although metal hydrides, such as $LiAlH_4$ and Bu^i_2AlH, can be used as the reducing agent,[2] the cost and functional group compatibility of metal hydride reagents often become a problem. Typical metals, such as lithium, sodium, and zinc, can be also used as the reducing agent for the hydrogenation of carbon–carbon π-systems in the presence of protic reagents, such as amines, alcohols, acids, and water. However, these reagents are mainly used in the selective reduction of alkynes to alkenes.[2] Catalytic transfer hydrogenation using simple alcohols, such as MeOH and Pr^iOH, and transition metal catalysts is an attractive method since it does not require pressurized conditions and expensive reagents.[3] Recently, Shirakawa, Hayashi, and co-workers have reported the hydrogenation of alkynes to alkenes using D_2O or H_2O as a hydrogen source and hexamethyldisilane as a reducing agent in the presence of palladium catalyst.[4] Here, we report a rhodium-catalyzed hydrogenation of olefins including α,β-unsaturated ketones using H_2O or D_2O as hydrogen source and zinc metal as a reducing agent.

The hydrogenation of olefins (1.0 mmol) was performed in a Schlenk tube in the presence of $[Rh(cod)Cl]_2$ (2.0 mol %) and zinc powder (2.0 mmol) in water (0.4 mL) and 1,4-dioxane (2.0 mL) at 90 °C for 20 h.[5] No reaction was observed in the absence of rhodium catalyst. Typical results are summarized in Table 1. The terminal olefins including aromatic and aliphatic ones afforded the saturated products in a quantitative yield (entries 1–4). No olefin isomerized product was observed in the case of aliphatic olefins. The reactions of internal *trans*-olefins, such as *trans*-β-methylstyrene and *trans*-stilbene, afforded the reduced products in moderate yields of 53% and 33%, respectively (entries 5 and 6). On the other hand, the hydrogenation of *cis*-stilbene proceeded smoothly affording the product in a quantitative yield (entry 7). The reaction of indene also proceeded to afford indan in 62% yield (entry 8).
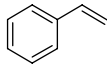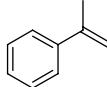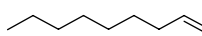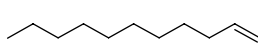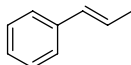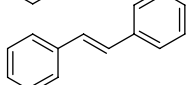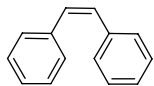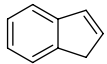
α,β-Unsaturated ketones including cyclic ones also underwent the present hydrogenation. In these cases, 1,4-reduced products were obtained selectively and no alcohol product was observed. Typical results are summarized in Table 2. The reactions of linear enones examined afforded the corresponding ketones in a quantitative yield (entries 1–3). Cyclic enones, such as 2-cyclohexenone and 3-methyl-2-cyclohexenone also afforded the corresponding ketones in a quantitative yield (entries 4 and 5). However, the reaction of 3,5,5-trimethyl-2-cyclohexenone gave the product in a low yield of 15% (entry 6). In this case, a steric hindrance of the three methyl groups would slow the reaction.

The present hydrogenation can also be applicable to the deuteration reaction using D_2O instead of water. Thus, the reaction of 1,3-diphenyl-2-propen-1-one in the presence of D_2O afforded the 2,3-dideuterated ketone in a

Table 1. Rhodium-catalyzed hydrogenation of olefins with water and zinc metal[a]

$$R^1{\diagdown}{=}{\diagdown}R^2 \xrightarrow[\text{Zn, H}_2\text{O, 1,4-dioxane,}\ 90\ °\text{C, 20 h}]{[\text{RhCl(cod)}]_2\ (2\ \text{mol}\%)} R^1{\diagdown}{\diagdown}R^2$$

Entry	Substrate	Yield[b] (%)
1		99
2		99
3		99
4		99
5		53
6		33
7		99
8		62

[a] The reaction was carried out in 1,4-dioxane (2 mL) at 90 °C for 20 h using olefins (1 mmol), Zn (2 mmol), H_2O (0.4 mL) in the presence of $[\text{Rh(cod)Cl}]_2$ (0.02 mmol).
[b] Isolated yield.

Table 2. Rhodium-catalyzed hydrogenation of α,β-unsaturated ketones with water and zinc metal[a]

$$R^1{\diagup}{=}{\diagup}\overset{\text{O}}{\underset{}{\text{C}}}R^2 \xrightarrow[\text{Zn, H}_2\text{O, 1,4-dioxane,}\ 90\ °\text{C, 20 h}]{[\text{RhCl(cod)}]_2\ (2\ \text{mol}\%)} R^1{\diagdown}{\diagdown}\overset{\text{O}}{\underset{}{\text{C}}}R^2$$

Entry	Substrate	Yield[b] (%)
1		99
2		99
3		99
4		99
5		99
6		15

[a] The reaction was carried out in 1,4-dioxane (2 mL) at 90 °C for 20 h using olefins (1 mmol), Zn (2 mmol), H_2O (0.4 mL) in the presence of $[\text{Rh(cod)Cl}]_2$ (0.02 mmol).
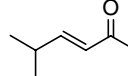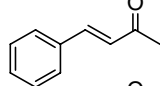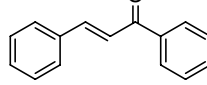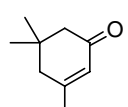[b] Isolated yield.

quantitative yield (Eq. 1). However, in the reaction of simple olefins such as styrene using D_2O, the scrambling of deuterium occurred giving a mixture of mono-, di-, and tri-deuterated products. The stereochemistry for the introduced deuterium atoms was determined using 3,5,5-trimethyl-2-cyclohexenone, indicating that the *syn:anti* ratio of the product was 1:1 (Eq. 2).

$$\text{Ph}{\diagup}{=}{\diagup}\overset{\text{O}}{\underset{}{\text{C}}}\text{Ph} \xrightarrow[\text{Zn, D}_2\text{O, 1,4-dioxane,}\ 90\ °\text{C, 20 h}]{[\text{RhCl(cod)}]_2\ (2\ \text{mol}\%)} \text{Ph}\overset{\text{D}}{\underset{\text{D}}{\diagup}}\overset{\text{O}}{\underset{}{\text{C}}}\text{Ph} \quad (1)$$

99 %

$$\xrightarrow[\text{Zn, D}_2\text{O, 1,4-dioxane,}\ 90\ °\text{C, 20 h}]{[\text{RhCl(cod)}]_2\ (2\ \text{mol}\%)} \quad (2)$$

23 %, *syn:anti* = 1:1
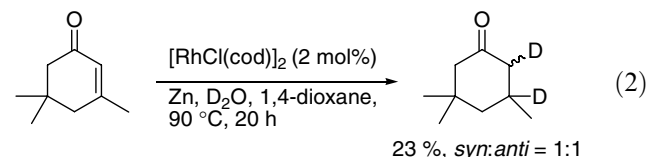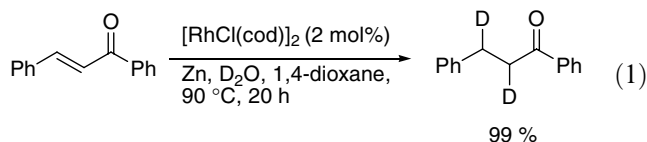
From the results of the deuteration experiments using D_2O, we believe that the reaction pathway involves the generation of a trivalent monodeuteriorhodium intermediate and the addition of the monodeuteriorhodium intermediate to a carbon–carbon double bond. A possible reaction pathway for simple olefins is shown in Scheme 1. The oxidative addition of D_2O to a rhodium(I) complex **A** generates a trivalent monodeuterio-

rhodium complex **B**.[6] The coordination of an olefin to **B** generates an η^2-complex **C** followed by the generation of a rhodium adduct **D**. In this step, the reversible formation of the η^2-complex **C** causes the scrambling of deuterium. The hydration of **D** by D_2O gives the hydrogenation product and a trivalent deuterioxy rhodium complex **E**. Finally, the reduction of **E** by zinc metal regenerates the monovalent rhodium complex **A**. In the cases of α,β-unsaturated ketones (Scheme 2), a rhodium adduct **F** quickly converts to an oxa-π-allyl rhodium complex **G** or a rhodium enolate **H**. Complex **G** or **H** easily hydrated without the reversible reaction and scrambling of deuterium, to give a *syn/anti* mixture of dideuterated product. An alternative pathway, which involves the generation of hydrogen gas from zinc metal and water, and usual hydrogenation with the hydrogen gas catalyzed by a rhodium complex cannot be completely ruled out. However, the generation of hydrogen gas was not observed during the reaction equipped with a gas burette.

In conclusion, the rhodium-catalyzed hydrogenation of olefins with water and zinc metal is described. Not only simple alkenes but also α,β-unsaturated ketones underwent the hydrogenation, affording saturated ketones selectively. The present reaction provides a simple and easy way for the hydrogenation and deuteration of olefins without expensive reagents and pressurized conditions.
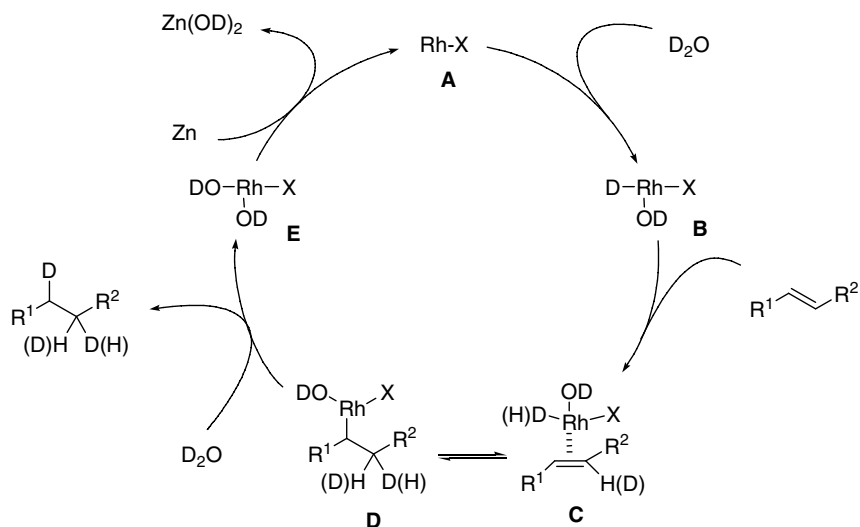
Scheme 1. A possible reaction pathway for the rhodium-catalyzed hydrogenation of olefins with water and zinc metal.
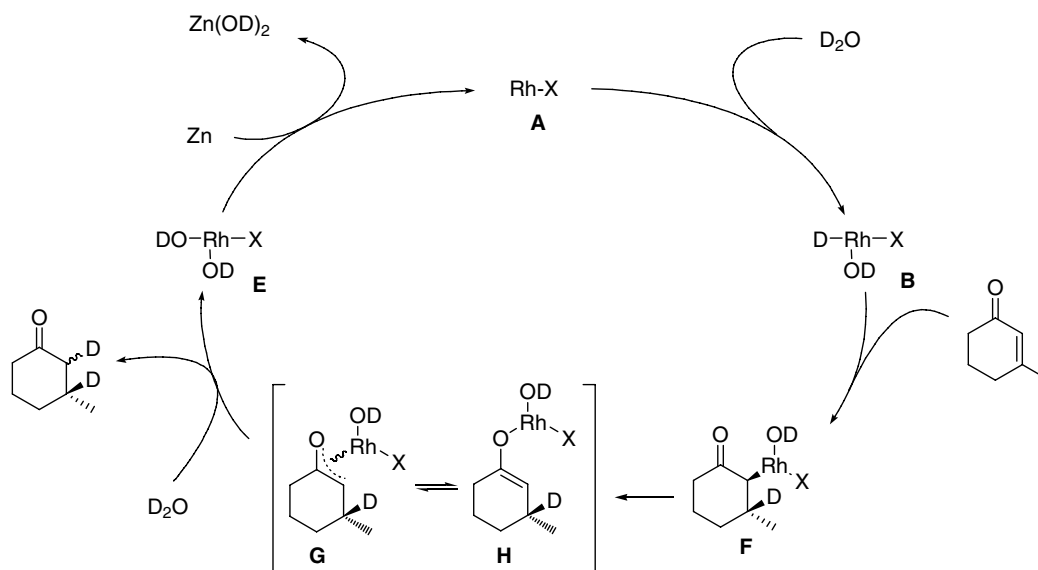
Scheme 2. A possible reaction pathway for the rhodium-catalyzed hydrogenation of α,β-unsaturated ketones with water and zinc metal.

References and notes

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5. Representative procedure: A mixture of olefin (1.0 mmol), [Rh(cod)Cl]₂ (0.02 mmol), and zinc powder (75–157 μm, 2.0 mmol) in water (0.4 mL) and 1,4-dioxane (2.0 mL) was stirred at 90 °C for 20 h under N₂ atmosphere. After the solvent was removed under reduced pressure, the residue was purified by silica-gel flash chromatography.
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