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Pages: 6

Ruthenium-Catalyzed Conjugate Hydrogenation of α,β-Enones by in situ Generated Dihydrogen from Paraformaldehyde and Water

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Notwithstanding that the highly selective hydrogenation of α , β -enones to allylic alcohols can be realized by using Noyori's Ru bifunctional system, the selective reduction of the C=C bonds in α , β -enones without touching the C=O bonds still lacks a general, simple, and efficient procedure.

Introduction

The conjugate reduction of α,β -enones is a very important synthetic transformation because^[1] α,β -enones can be easily prepared by many simple procedures^[2] and because the corresponding reduced products are interesting substructures for many pharmaceutically active molecules (Figure 1).^[3] Reduction systems such as dissolving metals^[1a] and metal hydrides^[1b] require cumbersome reagents, which has limited their synthetic applications. Over the past decades, conjugate transfer hydrogenations catalyzed by transition-metal complexes^[4] and organocatalysis^[5] have been continuously explored.



Figure 1. Selected bioactive molecules with the 1,4-diaryl ketone structures.

Catalytic hydrogenation is always reckoned as the most clean and efficient reduction method for modern organic synthesis. The selective hydrogenation of either the olefin or the ketone group in α,β -enone motifs can be challenging in some situations. In the 1990s, Noyori et al. selectively hydrogenated the carbonyl group in α,β -enones by using Ru–diphosphine–diamine bifunctional catalysts.^[6] Although the hydrogenation of C=C bonds is usually thermodynamically favored for α,β -enones, careful control over the Ruthenium-catalyzed conjugate hydrogenation of various α,β -enones to saturated ketones with high selectivity was investigated. The most important feature of this procedure was that hydrogen in situ generated from paraformaldehyde (or formalin) and water was employed as the reductant.

reaction conditions or special catalysts are often needed.^[7] Likely, heterogeneous hydrogenation (such as Pd/C) often leads to the over-reduction or even hydrogenolysis of the C=O groups in benzyl positions. Besides, some easily reducible groups such as aryl halogens and nitro and nitrile groups may not be tolerated.

Ruthenium-catalyzed homogeneous hydrogenation of alkenes and ketones is known for its high reactivity and selectivity.^[8] For safety and operation reasons, the use of in situ generated hydrogen without an autoclave device is a very promising alternative method for small-scale reactions in organic laboratories. Nowadays, hydrogen production from simple molecules such as water, formic acid, and alcohols is an ever-growing topic from the point of view of new, clean energy.^[9] More recently, Prechtl and co-workers reported the selective and mild production of hydrogen from water and formaldehyde with the use of [RuCl₂(pcymene)]₂ as the catalyst.^[10] They proposed that the ruthenium species could catalyze H/D scrambling between D₂O and the C-H bonds in HOCH₂OH, and in addition the dehydrogenation of deuterated methanediol would produce a mixture of D₂, H₂, and HD through the deuterated formic acids. Their procedure provided an elegant way to produce hydrogen from small molecules. However, the controlled generation of hydrogen from paraformaldehyde and water has seldom been applied in hydrogenation reactions.

Paraformaldehyde is an inexpensive and readily available C1 block that has been used in many organic synthesis^[11] and transition-metal-catalyzed transformations.^[12] For example, it has been used as a syngas equivalent in rhodium-catalyzed olefin/alkyne hydroformylations^[13] and in palladium-catalyzed carbonylations.^[14] To the best our knowledge, very few examples have been reported in which paraformaldehyde is used as the hydrogen donor in transitionmetal-catalyzed transfer hydrogenations.^[15] In comparison to formic acid, which is a pungent and corrosive liquid that is usually used in large excess amounts, paraformaldehyde

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Pages: 6

SHORT COMMUNICATION

is a more stable and easier-to-handle solid. Herein, we wish to report the ruthenium-catalyzed selective hydrogenation of the C=C bonds in α , β -enones by using paraformaldehyde and water as the in situ hydrogen generator.

Results and Discussion

At the outset, we performed the reaction with chalcone (1a) as the standard substrate and paraformaldehyde as the reductant to optimize the reaction conditions (Table 1). Upon heating a mixture of **1a**, paraformaldehyde (5 equiv.), K_2CO_3 (1 equiv.), and $RuCl_2(PPh_3)_3$ (2 mol-%) at 120 °C under an atmosphere of argon in H₂O, the conversion was greater than 99% but the yield of 2a was only 70% (Table 1, entry 1). Next, we performed the reaction in mixed toluene/ water solvents with different ratios (Table 1, entries 2-5). To our satisfaction, 2a was obtained in almost quantitative yield in the toluene/ $H_2O = 10$ system (Table 1, entry 4). Control experiments showed that 1 equivalent of K_2CO_3 was necessary for the reaction (Table 1, entries 6-9). Other solvents such as acetonitrile, dioxane, and DMF were much less efficient for the selective reduction of 1a to 2a (Table 1, entries 10-12). The catalyst formed in situ from RuCl₃ and PPh₃ also proved effective for this reduction (Table 1, entry 13). Interestingly, the reaction also produced 2a in 95% yield in the presence of [Ru(p-cymene)Cl₂]₂ (2 mol-%) under phosphine-free conditions (Table 1, entry 14). Upon replacing the ruthenium catalyst with Wilkinson catalyst or PdCl₂(PPh₃)₃, the conversion of **1a** was rather low (Table 1, entries 15 and 16). Finally, the optimized conditions included the use of $RuCl_2(PPh_3)_3$ as the catalyst, K_2CO_3 as the base, and toluene/ $H_2O = 10$ as the solvent at a reaction temperature of 120 °C.

Table 1. Optimization of the conjugate reduction of chalcone (1a).^[a]

With the optimized conditions in hand, we next extended the substrates to other substituted α,β -enones. Various substituted chalcones were smoothly reduced to their corresponding saturated ketones in good yields (Table 2). Notably, aryl halides such as chloro (see compound 1e), iodo (see compound 1d), and bromo (see compound 1f) were well tolerated and no dehalogenation was observed in these cases. The aryl carbon halides in these products were further converted into some versatile drug-like molecules through palladium-catalyzed couplings. Furthermore, nitro (see compound 1c) and nitrile (see compound 1i) groups, which are easily reduced under heterogeneous hydrogenation conditions, remained untouched with this procedure. Substituents ortho to either the keto group or the alkene had no clear effect on the efficiency of the reaction (see compound 1g). The ferrocenyl chalcone (see compound 1j) and pentamethyl chalcone (see compound 1k) were also reduced to their saturated forms in good yields. α , β -Enones with heterocycles such as furan, (benzo)thiophene, indole, and pyrrole were also reduced by this method without difficulty. If R¹ was an alkyl groups such as cyclopropanyl (see compound 1q), 2q was obtained in 87% yield. Cyclic enones such as chromone (1r) was reduced to chromane (2r) in excellent yield. The two conjugated C=C bonds in dibenzylideneacetone (1s) were selectively saturated in 84% yield. If there were two cumulative C=C bonds in the enone substrate, as in 1t, no conversion was observed upon using RuCl₂(PPh₃)₃ as the catalyst. However, upon using $[Ru(p-cymene)Cl_2]_2$ as the catalyst, a mixture of two possible products was obtained. Moreover, the trisubstituted alkenes in 1u and 1v were also reduced but in lower yields. The α,β -unsaturated ester methyl cinnamate (1w) was reduced to the saturated ester under the same conditions.

$\frac{1}{1a} \xrightarrow{Ph} + (CH_2O)_n \xrightarrow{cat.}_{base} Ph \xrightarrow{Ph} Ph$					
Entry	Catalyst ^[b] (mol-%)	Base (equiv.)	Solvent	Conversion ^[c] [%]	Yield ^[c] [%]
1	A (2)	$K_2CO_3(1)$	H ₂ O	>99	70
2	$\mathbf{A}(2)$	$K_{2}CO_{3}(1)$	$toluene/H_2O = 2$	>99	86
3	$\mathbf{A}(2)$	$K_{2}CO_{3}(1)$	$toluene/H_2O = 5$	>99	91 (13 ^[d])
4	A (2)	$K_2CO_3(1)$	$toluene/H_2O = 10$	>99	97 (95 ^[e])
5	$\mathbf{A}(2)$	$K_{2}CO_{3}(1)$	$toluene/H_2O = 10$	$>99^{[f]}(3^{[g]})$	95 ^[e]
6	A (2)	K_2CO_3 (0.4)	$toluene/H_2O = 10$	>99	88
7	A (2)	KOH (1)	$toluene/H_2O = 10$	>99	89
8	$\mathbf{A}(2)$	$Na_2CO_3(1)$	$toluene/H_2O = 10$	23	4
9	A (2)	$Et_3N(1)$	$toluene/H_2O = 10$	49	32
10	A (2)	$K_2CO_3(1)$	$MeCN/H_2O = 10$	32	20
11	A (2)	$K_2CO_3(1)$	$dioxane/H_2O = 10$	41	36
12	A (2)	$K_2CO_3(1)$	$DMF/H_2O = 10$	>99	81
13	C (2)	$K_2CO_3(1)$	$toluene/H_2O = 10$	96	91
14	D (2)	$K_2CO_3(1)$	$toluene/H_2O = 10$	>99	95
15	E (2)	$K_2CO_3(1)$	$toluene/H_2O = 10$	24	22
16	F (2)	$K_2CO_3(1)$	$toluene/H_2O = 10$	<1	_

[a] Reaction conditions: 1a (52.1 mg, 0.25 mmol), (CH₂O)_n (37.5 mg, 1.25 mmol) in solvent (1.8 mL) for 16 h at 120 °C. [b] Catalyst: A = RuCl₂(PPh₃)₃; B = Ru₃(CO)₁₂ (3%) + PPh₃ (10%); C = RuCl₃·3H₂O (2%) + PPh₃ (6%); D = [Ru(*p*-cymene)Cl₂]₂; E = RhCl(PPh₃)₃; F = PdCl₂(PPh₃)₂. [c] Determined by GC by using *n*-C₁₆H₃₄ as the internal standard. [d] In air. [e] Yield of isolated product. [f] 37% Aqueous formalin solution (92 μ L, 1.25 mmol) was used. [g] Trioxin (37.5 mg, 1.25 mmol) was used.



Ruthenium-Catalyzed Conjugate Hydrogenation of α,β -Enones

Table 2. Substrate scope for the conjugate reduction of α,β -enones.^[a]



[a] All reactions were performed with 0.25 or 0.3 mmol of the substrate. [b] $(CH_2O)_n$ (4 equiv.) was added. [c] $[Ru(p-cymene)Cl_2]_2$ was used as the catalyst and an approximately 2:1 mixture of 1,5-diphenylpent-4-en-1-one/1,5-diphenylpentan-1-one was obtained. [d] GC yield. [e] Determined by GC, 60% conversion.

However, the reduction of unfunctionalized alkenes such 4phenylbutene (1x) proceeded much more slowly, which indicated that the carbonyl group probably participated in coordination to the ruthenium atom during the hydrogenation.

Next, we tried to gain some insight into the mechanism of this conjugate reduction process. First, a mixture of chalcone and deuterated paraformaldehyde was heated under the standard conditions in toluene/ D_2O (10:1); 62% deuteration in the α position of 2a was observed, which was due to the acidity of the proton α to the ketone group. Furthermore, no deuteration occurred at the much less acidic β position [Scheme 1, Equation (1)]. Upon using non-deuterated paraformaldehyde instead [Scheme 1, Equation (2)], 20% deuteration at the β position was observed. These results suggested that the hydrogen atom transferred to 1a partially originated from paraformaldehyde and partially from water. Upon using deuterated paraformaldehyde and H₂O, we found a much higher ratio of hydrogen in both the α and β positions of the products [Scheme 1, Equation (3)]. This is also in agreement with the observation from Prechtl and co-workers: the dehydrogenation of $(CD_2O)_n$ in H₂O produced mainly H₂, and dehydrogenation of $(CH_2O)_n$ in D₂O produced D₂, HD, and H₂ in

decreasing abundance.^[10] The final decomposition product of paraformaldehyde was CO₂, which could be detected by bubbling gas into lime water (see Figure S1 in Supporting Information for details).

$$\mathbf{1a} + (C\mathbf{D}_2 O)_n + \mathbf{D}_2 O \xrightarrow{\text{toluene}} Ph \xrightarrow{\text{O}} H/\mathbf{D} = 50:50$$

$$H/\mathbf{D} = 50:50$$

$$\mathbf{1a} + (CH_2O)_n + \mathbf{D}_2O \xrightarrow{\text{toluene}} Ph \xrightarrow{O} H/D=80:20 \\ H/D=53:47 + CO_2$$
(2)

$$\mathbf{1a} + (\mathbf{CD}_{2}\mathbf{O})_{n} + \mathbf{H}_{2}\mathbf{O} \xrightarrow{\mathbf{H}_{2}\mathbf{O}} \mathbf{Ph} \xrightarrow{\mathbf{O}} \mathbf{H/D} = 57:36$$

$$\mathbf{H/D} = 57:36$$

Scheme 1. Deuterated experiment (the reactions were performed under the conditions of entry 5 in Table 1).

On the basis of the above analysis and experiments, we believe that the conjugate reduction is most probably a ruthenium-catalyzed hydrogenation process. The hydrogen atom transferred to the products came from decomposition of paraformaldehyde and water in the presence of the ruthenium catalyst; this was further verified by an experiment in a two-chamber reactor (Scheme 2, see Figure S2 in Sup-

SHORT COMMUNICATION

porting Information for details). In chamber B, **1a** was still reduced to **2a** in 76% yield, so we confirmed that gaseous hydrogen was produced in chamber A by considering that $RuCl_2(PPh_3)_3$ is a good catalyst for olefin hydrogenation.^[16] The high selectivity of our procedure lied in the fact that only 10 equiv. of hydrogen was produced at most, and accordingly, the partial pressure of H₂ was estimated to be no more than 2 kPa under our optimized conditions (Table 1, entry 5).^[17]





Scheme 2. Reduction of 1a in a two-chamber reactor.

Conclusions

In conclusion, we realized the chemoselective hydrogenation of α,β -enones by using a cheap and commercially available ruthenium complex with the use of paraformaldehyde and water as the hydrogen source. In situ generated hydrogen was experimentally validated through deuterated experiments and a two-chamber reaction. With this new method, we were able to realize the selective hydrogenation of olefins in α,β -enones without the manipulation of hazardous high-pressure H₂. In comparison to traditional hydrogen donors such as the HCOOH–Et₃N azeotrope, this new combination is cheaper and easier to handle. The employment of such in situ generated hydrogen in other catalytic hydrogenation reactions is underway in our group.

Experimental Section

General Procedure for the Conjugate Hydrogenation Reaction: An oven-dried pressure tube (10 mL) was charged with **1a** (52 mg, 0.25 mmol), RuCl₂(PPh₃)₃ (4.79 mg, 10 µmol), paraformaldehyde (37.5 mg, 1.25 mmol), and K₂CO₃ (35 mg, 0.25 mmol). The pressure tube was then transferred into a larger Schlenk tube and was vacuumed and purged with argon (3×). Next, toluene (1.6 mL) and distilled water (0.16 mL) were added by syringe under argon flow before the pressure tube was sealed with a Teflon cap. After that, the mixture in the pressure tube was stirred and heated at 110 °C in an alloy block for 18 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Desired product **2a** was purified by column chromatography (pentane/ ethyl acetate = 30) and obtained in 95% yield.

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Ruthenium-Catalyzed Conjugate Hydrogenation of a, β-Enones

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- [17] The theoretical partial pressure of $P(H_2)$ was calculated according to the equation of state of an ideal gas $P(H_2) = nRT/V$, in which T = 393 K (120 °C), V = 20 cm³, $n(H_2) = 12.5 \times 10^{-3}$ mmol; therefore, $P(H_2) = 2042$ Pa.

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Hydrogenation

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Ruthenium-Catalyzed Conjugate Hydrogenation of α,β -Enones by in situ Generated Dihydrogen from Paraformaldehyde and Water

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Dihydrogen (H₂) is produced from paraformaldehyde and water in the presence of simple $RuCl_2(PPh_3)_3$ as a catalyst. The in situ generated hydrogen is utilized in the selective hydrogenation of olefins in α , β enones catalyzed by the same catalyst. This high-pressure-free procedure shows very high selectivity and generality.