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Journal of Organometallic Chemistry 692 (2007) 3065–3069
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

An efficient catalytic system for the hydrogenation of quinolines

Sheng-Mei Lu, Xiu-Wen Han, Yong-Gui Zhou *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

Received 16 January 2007; received in revised form 16 March 2007; accepted 22 March 2007
Available online 28 March 2007

Abstract

A new catalytic system ([Ru(*p*-cymene)Cl_2]$_2$/I_2) has been developed for the hydrogenation of quinoline derivatives with high reactivity. For the 2-methyl-quinoline, the hydrogenation reaction can proceed smoothly at an S/C of 20,000/1 with complete conversion. The iodine additive is important for the reactivity.

Keywords: Quinolines; Hydrogenation; Iodine

1. Introduction

Transition metal-catalyzed hydrogenation of heteroaromatic compounds is one of the most efficient methods for the construction of heterocyclic skeletons, and only a few promising progress has been achieved [1]. Tetrahydroquinoline derivatives are important synthetic intermediates [2] and structural unit of alkaloids [3]. Direct hydrogenation of quinolines would be the most convenient route to obtain tetrahydroquinoline derivatives. Many efforts have been made toward the development of homogenous hydrogenation of quinolines using Rh, Ru or Ir catalyst in an achiral version. Fish and coworkers reported the first hydrogenation of quinolines using 10 mol% ruthenium complexes at high temperature (150 °C for [$H_4Ru_4(CO)_{12}$] and 180 °C for [$Ru(Cl)_2(CO)_2(PPh_3)_2$]) [4]. Subsequently, they employed [$(PPh_3)_3RhCl$] and [$Cp^*Rh(CH_3CN)_2]^{2+}$ as the catalyst precursors to hydrogenate quinoline at slightly lower temperature (85 and 40 °C) [5]. Murahashi and coworkers reported rhodium-catalyzed hydrogenation of a series of quinoline derivatives under water–gas shift conditions at 150 °C [6]. Watanabe described the transfer hydrogenation of quinoline with formic acid in the presence of 0.25 mol% [$RuCl_2(PPh_3)_3$] [7]. However, high conversion was obtained only at high temperature (>150 °C). In 2004, Fujita and Yamaguchi reported Cp*Ir-catalyzed regio- and chemo-selective transfer hydrogenation of quinolines using 2-propanol as a hydrogen donor under reflux conditions [8]. Very recently, an organocatalytic transfer hydrogenation of quinolines and its asymmetric version were also reported by Rueping et al. [9]. Among the above catalytic systems for the hydrogenation of quinolines, the catalyst loading is high, and the reaction condition is harsh. Therefore, an efficient catalytic system for hydrogenation of quinolines under mild conditions is highly desirable.

Recently we developed two asymmetric catalytic systems, [Ir(COD)Cl]$_2$/MeO–BiPhep/I_2 and [Ir(COD)Cl]$_2$/SegPhos/Li_2CO_3/$ClCO_2Bn$, for the hydrogenation of quinoline derivatives under mild conditions using iridium complexes [10]. With these catalysts, a variety of quinoline derivatives could be hydrogenated at room temperature under 600 psi of hydrogen. Based on these results, we envisaged the combination of iodine and other metal precursor such as ruthenium would be an efficient catalyst for the hydrogenation of quinolines. Herein, we report our work on the hydrogenation of quinolines with a new catalytic system ([Ru(*p*-cymene)Cl_2]$_2$/I_2/THF) under mild conditions.

* Corresponding author. Tel./fax: +86 411 84379220.
E-mail address: ygzhou@dicp.ac.cn (Y.-G. Zhou).

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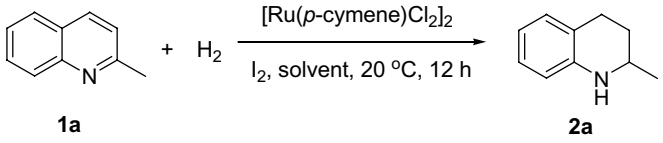
doi:10.1016/j.jorganchem.2007.03.032

2. Results and discussion

For our initial investigations on the hydrogenation of quinolines, 2-methylquinoline (**1a**) was selected as the model substrate and [Ru(*p*-cymene)Cl_2]$_2$/(rac)-MeO–BiPhep prepared in situ was employed as the catalytic system with a substrate:[Ru]:L:I_2 ratio of 100:1:1.1:5. When the reaction was operated in glovebox and then proceeded under 600 psi of hydrogen at 20 °C, 89% conversion was obtained with excellent chemoselectivity. Interestingly, when the above reaction was carried out in the absence of ligand, the reaction could also proceed with a slightly lower conversion (63%). This result renders us to think that the reaction can perform in air because [Ru(*p*-cymene)Cl_2]$_2$ is stable to air in solution. Therefore, we carried out the above reaction in air in the absence of ligand, and 54% conversion was obtained. Though the conversion is slightly lower than that in the glovebox, the process is operationally simple. As a consequence, we determined to study the reaction parameters in air with undistilled solvents.

First, we evaluated the effect of solvents on the conversion (Table 1). The results reveal that the conversion of the hydrogenation reaction is solvent dependent. The reactions in EtOAc, EtOH and THF could proceed smoothly to give the desirable product **2a** with full conversion (entries 5, 7, 9). However, in other solvents such as toluene, CH_2Cl_2, CH_3OH and *i*-PrOH, partial conversions were given (entries 3, 4, 6, 8). Utilizing THF as the solvent, the effect of hydrogen pressure was studied, lowering the hydrogen pressure to 300 psi had no clear effect on the conversion. However, only 20% conversion was obtained when the hydrogen pressure was further lowered to 100 psi.

Table 1
The effects of solvent and pressure on the conversion[a]

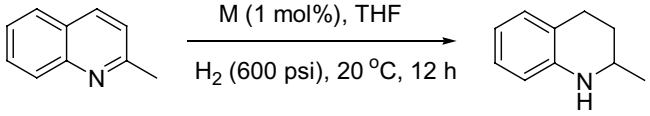


1a **2a**

Entry	Solvent	Press. (psi)	Convn.[b] (%)
1	Toluene	600	89[c]
2	Toluene	600	63[d]
3	Toluene	600	54
4	CH_2Cl_2	600	95
5	EtOAc	600	>95
6	CH_3OH	600	83
7	EtOH	600	>95
8	*i*-PrOH	600	90
9	THF	600	>95
10	THF	300	>95
11	THF	100	20

[a] Unless otherwise stated, reactions were performed under the air in 0.5 mmol scale, **1a**/[Ru(cymene)Cl_2]$_2$/I_2 = 100/0.5/5.
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] 1.1 mol% (rac)-MeO–BiPhep was added, operated in glovebox.
[d] Operated in glovebox.

Table 2
The effect of metal precursors on the conversion[a]



1a **2a**

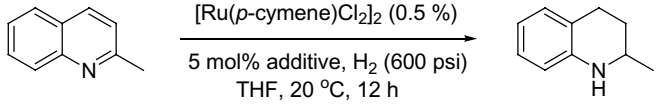
Entry	Metal precursor	Additive	Convn.[b] (%)
1	[Ru(*p*-cymene)Cl_2]$_2$	I_2	>95
2	[Ru(*p*-cymene)Cl_2]$_2$	No	<5
3	[Ru(*p*-cymene)I_2]$_2$	I_2	>95
4	[Ru(*p*-cymene)I_2]$_2$	No	48
5	[Ru(benzene)Cl_2]$_2$	I_2	>95
6	[Ru(benzene)Cl_2]$_2$	No	<5
7	[Ru(COD)Cl_2]$_x$	I_2	<5
8	[Ru(COD)Cl_2]$_x$	I_2	<5[c]
9	Ru/C	No	<5
10	Ru/C	I_2	<5

[a] Unless otherwise stated, reactions were performed under the air in 0.5 mmol scale, **1a**/M/I_2 = 100/1/5, 3 mL THF.
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] 1.1 mol% of (rac)-MeO–BiPhep was added.

Under 600 psi hydrogen pressure in THF, the effect of other ruthenium precursors on conversion was investigated. The results are summarized in Table 2. In the presence of catalytic amount of iodine, when [Ru(*p*-cymene)Cl_2]$_2$, [Ru(*p*-cymene)I_2]$_2$ and [Ru(benzene)Cl_2]$_2$ were used as the ruthenium precursors, the reactions proceeded with full conversion (entries 1, 3, 5). However, without iodine, only [Ru(*p*-cymene)I_2]$_2$ gave a conversion of 48% (entry 4), the other two did not lead to observable product (entries 2 and 6). The results showed that the additive of iodine is crucial for the reaction. However, using [Ru(COD)Cl_2]$_x$ as the catalyst, the hydrogenation reaction did not proceed at all even in the presence of iodine (entry 7). Considering the low solubility of [Ru(COD)Cl_2]$_x$, the ligand (*rac*)-MeO–BiPhep was added, but the reaction did not occur (entry 8). Comparing the above results, the arene moiety of the metal complexes is also essential for the reactivity of the catalyst. When Ru/C was used as the catalyst, the reaction did not occur with or without iodine (entries 9, 10). It indicated that the hydrogenation of quinoline by [Ru(*p*-cymene)Cl_2]$_2$/I_2 might not be a heterogeneous reduction.

As the iodine additive is necessary for the high conversion in the above reaction, the effect of other additives [11] on the hydrogenation is investigated under the above optimal conditions, and the results are shown in Table 3. The alkali metal iodide salts such as KI and LiI could also promote the reaction (entries 1, 3) to give full conversion, but NaI, LiBr or LiCl gave low conversion (entries 2, 4, 5). The conversion was improved to 85% using [Ru(*p*-cymene)I_2]$_2$ instead of [Ru(*p*-cymene)Cl_2]$_2$ in the presence of LiCl(entry 6). The conversion was full when NIS was employed (entry 7), but the NBS only afforded 50% conversion (entry 8). In summary, the optimized conditions for hydrogenation of quinolines are [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF/H_2(600 psi).

Table 3
The effect of additives on the conversion of the hydrogenation reaction[a]



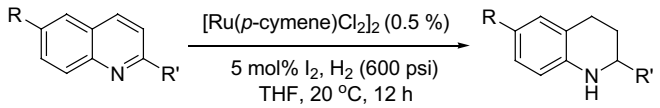
1a 2a

Entry	Additive	Convn.[b] (%)
1	KI	>95
2	NaI	52
3	LiI	>95
4	LiBr · H_2O	15
5	LiCl	<5
6[c]	LiCl	85
7	NIS	>95
8	NBS	50

[a] Unless otherwise stated, reactions were performed under the air in 0.5 mmol scale, **1a**/[Ru(cymene)Cl_2]$_2$/I_2 = 100/0.5/5, 3 mL THF.
[b] Determined by ^{1}H NMR analysis of the crude products.
[c] [Ru(cymene)I_2]$_2$ was used instead of [Ru(cymene)Cl_2]$_2$.

To assess the substrate scope of [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF catalyst system, a variety of substituted quinoline derivatives were hydrogenated under the optimized conditions. As shown in Table 4, 2-alkyl-substituted quinolines were hydrogenated smoothly to give the corresponding 1,2,3,4-tetrahydroquinolines with full conversions and in 82–90% isolated yields (**2a**–**e**). For the 2,6-disubstituted quinoline, the reaction proceeded well (**2f**, 90% yield). However, for the 2-phenyl-quinoline, the hydrogenation reaction did not occur at all, and this might be due to the bulkiness of the phenyl group at 2-position of the quinoline. The hydroxyl group was well tolerated with this catalyst system (entry 8). Simple quinoline (**1i**) was also tested with the [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF catalyst system, but the conversion was not complete (convn: 90%) even at 50 °C, the reason might be relatively high coordination ability of hydrogenation product tetrahydroquinoline.

Table 4
Ruthenium-catalyzed hydrogenation of quinolines[a]

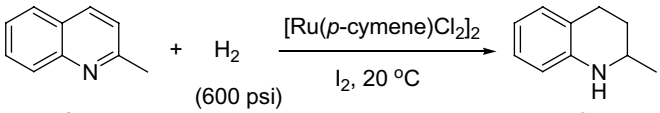


1 2

Entry	R and R′ of **1**	Product	Yield (%)[b]
1	H/Me (**1a**)	**2a**	90
2	H/Et (**1b**)	**2b**	90
3	H/*n*-Butyl (**1c**)	**2c**	82
4	H/Phenethyl (**1d**)	**2d**	83
5	H/3,4-$(MeO)_2C_6H_3(CH_2)_2$ (**1e**)	**2e**	80
6	F/Me (**1f**)	**2f**	90
7	H/Ph (**1g**)	**2g**	<5
8	H/*c*-$C_6H_{10}(OH)CH_2$-(**1h**)	**2h**	76
9	H/H (**1i**)	**2i**	64[c]

[a] Reaction conditions: 0.5 mmol scale, Quinolines/[Ru(*p*-cymene)Cl_2]$_2$/I_2 = 100/0.5/5, 3 mL THF, 600 psi H_2.
[b] Isolated yield based on the quinolines by column chromatography.
[c] Conversion is 90%.

Table 5
The effect of S/C on the conversion of the hydrogenation reaction[a]



1a 2a

Entry	S/C	Solvent	mL	Time (h)	Convn.[b] (%)
1	1000	THF	12	12	>95
2	1000	EtOAc	12	12	>95
3	1000	EtOH	12	12	>95
4	10,000	THF	30	12	>95
5	10,000	EtOAc	30	24	96
6	10,000	EtOH	30	24	18
7	20,000	THF	40	24	>95

[a] Unless otherwise stated, reactions were performed under the air using 0.005 mmol [Ru(*p*-cymene)Cl_2]$_2$, 0.05–0.1 mmol I_2.
[b] Determined by ^{1}H NMR analysis of the crude products.

For the 2-methylquinoxaline and 1-methylisoquinoline, this catalyst system is ineffective.

To evaluate further the catalytic efficiency of the [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF catalyst system, we investigated the substrate-to-catalyst (S/C) molar ratio on the conversion of this hydrogenation reaction. Using 2-methylquinoline as the substrate, the results were shown in Table 5. From the above results, we knew that the reaction in EtOH, EtOAc and THF proceeded completely at an S/C of 100/1. When we increased the S/C to 1000/1 in the presence of iodine [12], the conversions were also full in these three solvents. When the S/C was 10,000/1, 18% and 96% conversions were obtained in EtOH and EtOAc, respectively, within 24 h. However the reaction proceeded smoothly with complete conversion in THF within 12 h. Using THF as the solvent, we continued to increase the S/C to 20,000/1, the reaction proceeded completely in 24 h. It should be noted that all these reactions were carried out at 20 °C in air with undistilled solvents. These results indicate that the [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF catalyst system is very efficient for the hydrogenation of quinolines.

3. Summary

In summary, [Ru(*p*-cymene)Cl_2]$_2$/I_2/THF is effective catalyst for the hydrogenation of quinolines, and the reaction can be achieved with the S/C of 20,000/1 for the hydrogenation of 2-methylquinoline. The iodine additive is important for the high efficiency of the catalyst. This catalyst system provides a mild and effective method to synthesize tetrahydroquinoline derivatives. Further studies of its asymmetric version are in progress in our labortary [13].

4. Experimental

4.1. General considerations

Commercially available ruthenium complexes (Aldrich) [Ru(*p*-cymene)Cl_2]$_2$, [Ru(*p*-cymene)I_2]$_2$, [Ru(benzene)Cl_2]$_2$

and $[Ru(COD)Cl_2]_x$ were used as received. Iodine (Acros) was purchased and ground before use. Quinoxaline, quinoline and 2-methylquinoline were distilled before use. Other quinolines derivatives were prepared from 2-methylquinoline. The solvents used in the glovebox were purchased (Acros) and used directly. All the solvents used under the air were purchased (AR, Kermel company, China) and used directly without any purification. The conversion was determined by ^1H NMR analysis recorded at 400 MHz on a Bruker DRX-400 spectrometer. Hydrogenation reactions were performed with a stainless steel autoclave (300 mL internal volume). ^1H NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{TMS} = 0.00$ ppm or $CDCl_3$ (δ, 7.26 ppm).

4.2. Hydrogenation of 2-methyl-quinoline in the glovebox in the presence of ligand

In a glovebox, to a mixture of $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.0025 mmol) and (*rac*)-MeO–BiPhep (3.2 mg, 0.0055 mmol) was added dry THF (2 mL). To another mixture of I_2 (6.4 mg, 0.025 mmol) and 2-methyl-quinoline (72 mg, 0.5 mmol) was added THF (1 mL). Both of them were stirred at room temperature for 10 min, then the *in situ* prepared catalyst solution was added into the mixture of I_2 and substrate using a syringe. The hydrogenation was performed at room temperature under H_2 (600 psi) for 12 h. After carefully releasing the hydrogen, the reaction mixture was concentrated and the conversion was determined by ^1H NMR analysis.

4.3. Typical procedure for the hydrogenation of quinolines **1** under the air

In the air, to the reaction bottle A was added $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.0025 mmol) and 2 mL undistilled THF. The mixture was stirred until the solution is homogeneous. At the same time, to the reaction bottle B was added quinolines (0.5 mmol) and I_2 (6.4 mg, 0.025 mmol), followed by 1 mL THF. The mixture was stirred until the iodine is dissolved. Then to the reaction bottle B was added the solution of $[Ru(p\text{-cymene})Cl_2]_2$ of THF in bottle A. Then the resulting reaction mixture was placed in an autoclave. Finally the autoclave was pressurized to 600 psi hydrogen and stirred at 20 °C for 12 h. After carefully releasing the hydrogen, the reaction mixture was concentrated to afford the crude product. Purification was performed by a silica gel column eluted with hexane/EtOAc to give pure product.

*2-Methyl-1,2,3,4-tetrahydroquinoline (**2a**) [10]:* Yield: 90%, ^1H NMR (400 MHz, $CDCl_3$) 1.24 (t, $J = 6.5$ Hz, 3H), 1.62 (m, 1H), 1.96 (m, 1H), 2.81 (m, 2H), 3.42 (m, 1H), 3.50 (br, 1H), 6.49 (d, $J = 8.2$ Hz, 1H), 6.63 (m 1H), 6.98 (m, 2H).

*2-Ethyl-1,2,3,4-tetrahydroquinoline (**2b**) [10]:* Yield: 90%, ^1H NMR (400 MHz, $CDCl_3$) 0.95 (t, $J = 7.6$ Hz, 3H), 1.52 (m, 3H), 1.92 (m, 1H), 2.73 (m, 2H), 3.12 (m, 1H), 3.68 (br, 1H), 6.43 (d, $J = 8.2$ Hz, 1H), 6.56 (t, $J = 8.3$ Hz, 1H), 6.92 (m, 2H).

*2-Butyl-1,2,3,4-tetrahydroquinoline (**2c**) [10]:* Yield: 82%, ^1H NMR (400 MHz, $CDCl_3$) 0.96 (t, $J = 7.0$ Hz, 3H), 1.49 (m, 7H), 1.95 (m, 1H), 2.75 (m, 2H), 3.21 (m, 2H), 3.71 (br, 1H), 6.45 (d, $J = 8.2$ Hz, 1H), 6.59 (m, 1H), 6.97 (m, 2H).

*2-Phenethyl-1,2,3,4-tetrahydroquinoline (**2d**) [10]:* Yield: 83%, ^1H NMR (400 MHz, $CDCl_3$) 1.96 (m, 1H), 2.12 (m, 2H), 2.28 (m, 1H), 3.02 (m, 4H), 3.56 (m, 1H), 4.01 (br, 1H), 6.72 (d, $J = 8.2$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 7.25 (m, 2H).

*2-(3′,4′-Dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (**2e**) [10]:* Yield: 83%, ^1H NMR (400 MHz, $CDCl_3$) 1.65 (m, 1H), 1.81 (m, 2H), 1.98 (m, 1H), 2.67 (m, 4H), 2.77 (m, 1H), 3.28 (m, 1H), 3.85 (s, 3H), 3.86 (s, 3H), 6.44 (d, $J = 8.0$ Hz, 1H), 6.59 (m, 1H), 6.74 (m, 3H), 6.94 (m, 2H).

*6-Fluoro-2-mthyl-1,2,3,4-tetrahydroquinoline (**2f**) [10]:* Yield: 90%, ^1H NMR (400 MHz, $CDCl_3$) 1.13 (d, $J = 6.0$ Hz, 3H), 1.53 (m, 1H), 1.85 (m, 1H), 2.64 (m, 1H), 2.74 (m, 1H), 3.28 (m, 1H), 3.70 (br, 1H), 6.34 (m, 1H), 6.61 (m, 2H).

*1-(1,2,3,4-tetrahydroquinolin-2-ylmethyl)-cyclohexanol (**2h**) [10]:* Yield: 76%, ^1H NMR (400 MHz, $CDCl_3$) 1.24 (m, 2H), 1.53 (m, 14H), 1.74 (m, 1H), 2.67 (m, 1H), 2.78 (m, 1H), 3.50 (m, 1H), 6.39 (m, 1H), 6.49 (m, 1H), 6.87 (m, 2H).

*1,2,3,4-tetrahydroquinoline (**2i**) [10]:* Yield: 64%, ^1H NMR (400 MHz, $CDCl_3$) 1.93 (m, 2H), 2.76 (t, $J = 6.4$ Hz, 2H), 3.29 (t, $J = 5.2$ Hz, 2H), 3.79 (bs, 1H), 6.45 (m, 1H), 6.60 (m, 1H), 6.95 (m, 2H).

Acknowledgements

We are grateful for the financial support from National Science Foundation of China (20532050).

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[12] When the S/C is 1000/1, using KI and LiI as the additive, the conversions in THF are 37% and 34%, respectively.

[13] The asymmetric version of the present reaction was investigated briefly. The hydrogenation of **1a** was carried out using $[Ru(cymene)Cl_2]_2$ as the metal precursor with the following chiral ligands in THF in the presence of iodine: (*R*,*R*)-Me–DuPhos, (*R*)-MeO–BiPhep and (*R*)-BINAP. These reactions gave product 2a with good yields, but the enantioselectivities were very low (<2% ee).