ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2015, **51**, 7558

Received 9th March 2015,
Accepted 26th March 2015

DOI: 10.1039/c5cc01971k

www.rsc.org/chemcomm

Catalytic asymmetric hydrogenation of quinoline carbocycles: unusual chemoselectivity in the hydrogenation of quinolines†

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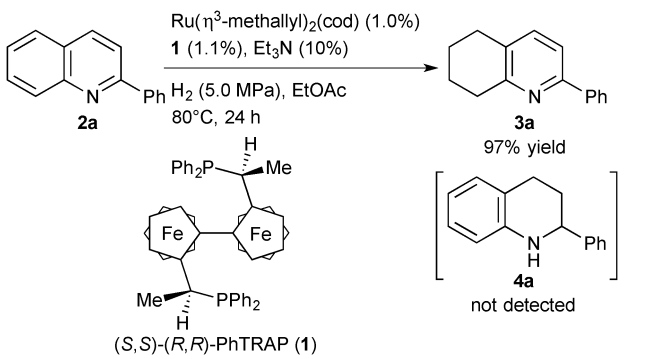
The reduction of quinolines selectively took place on their carbocyclic rings to give 5,6,7,8-tetrahydroquinolines, when the hydrogenation was conducted in the presence of a Ru(η³-methallyl)₂(cod)–PhTRAP catalyst. The chiral ruthenium catalyst converted 8-substituted quinolines into chiral 5,6,7,8-tetrahydroquinolines with up to 91 : 9 er.

Catalytic asymmetric hydrogenation of heteroarenes or arenes is an attractive approach for creating a chiral center on a 5- or 6-membered ring.[1] The potential usefulness has stimulated many chemists to develop chiral catalysts for the asymmetric reduction of heteroarenes during the last decade. Nowadays, asymmetric catalysis allows various heteroarenes to be converted to the fully or partly saturated chiral heterocycles with high enantiomeric excesses. As compared to heteroarenes, carbocyclic arenes have been unexplored as the substrates of the catalytic asymmetric hydrogenation, because they are highly stabilized with their aromaticity.[2,3] Overcoming the difficulty in breaking the aromaticity, Glorius successfully developed the asymmetric hydrogenation of the carbocycles in 6-alkyl-2,3-diphenylquinoxalines, which were converted to the corresponding 5,6,7,8-tetrahydroquinoxalines with up to 94 : 6 er.[4] Subsequently, we reported that substituted naphthalenes were hydrogenated with high enantioselectivities through the chiral catalyst, which is composed of ruthenium and *trans*-chelating chiral bisphosphine ligand, PhTRAP (**1**).[5,6]

Quinoline is the most studied substrate for the catalytic asymmetric hydrogenation of arenes.[7–9] Commonly, its pyridine ring was exclusively reduced to give optically active 1,2,3,4-tetrahydroquinoline, even when a chiral ruthenium complex was used as the catalyst.[10] Anomalistically, the carbocycle of quinoline is known to be selectively reduced with hydrogen in the presence of achiral PtO_2[11] or Chaudret's catalyst.[12] The stereoselective hydrogenation of quinoline carbocycles has been developed by using the platinum catalyst, but the reaction requires a stoichiometric chiral auxiliary to modify the substrate.[13] Here, we report a catalytic asymmetric hydrogenation of quinoline carbocycles to yield optically active 5,6,7,8-tetrahydroquinolines. The PhTRAP–ruthenium catalyst allows the hydrogenation of various 8-substituted quinolines to give the corresponding tetrahydroquinolines with good enantioselectivities.

We have developed highly enantioselective hydrogenation reactions of various heteroarenes with a chiral catalyst, the **1**–ruthenium complex.[14] In the course of our study on the asymmetric hydrogenation, the hydrogenation of 2-phenylquinoline (**2a**) was attempted by using the Ru(η³-methallyl)₂(cod)–**1**–Et_3N catalyst (Scheme 1). To our surprise, the dearomatization of **2a** exclusively took place on its carbocycle to afford 5,6,7,8-tetrahydroquinoline **3a** in 97% yield. No formation of **4a** was detected in the reaction. The unusual chemoselectivity stimulated us to develop the catalytic asymmetric hydrogenation of quinoline carbocycles.

The hydrogenation of quinoline-6-carboxylate **2b** was carried out under the reaction conditions indicated in Scheme 1 (Table 1, entry 1). Substrate **2b** was completely consumed within 24 h, but its pyridine moiety was selectively reduced to



Scheme 1 Ruthenium-catalyzed hydrogenation of **2a**.

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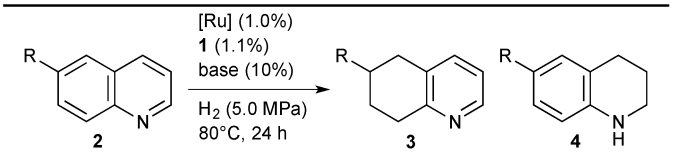
† Electronic supplementary information (ESI) available: Experimental details and analytical data. See DOI: 10.1039/c5cc01971k

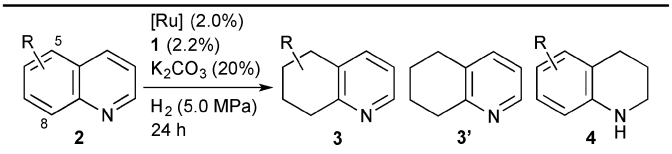
Table 1 Hydrogenation of 6-substituted quinolines[a]



Entry	2	Base	Solvent	3 : 4[b]	Er (3)[c]
1	**2b**	Et_3N	EtOAc	7 : 93	66 : 34
2	**2b**	—	EtOAc	7 : 93	66 : 34
3	**2b**	TMG[d]	EtOAc	30 : 70	67 : 33
4	**2b**	DBU	EtOAc	72 : 28	67 : 33
5	**2b**	K_2CO_3	EtOAc	88 : 12	67 : 33
6	**2b**	Cs_2CO_3	EtOAc	93 : 7[e]	65 : 35
7	**2b**	K_2CO_3	Toluene	8 : 92	66 : 34
8	**2b**	K_2CO_3	THF	64 : 36	70 : 30
9	**2b**	K_2CO_3	^{i}PrOH	93 : 7[f]	67 : 33
10	**2b**	DBU	^{i}PrOH	85 : 15	67 : 33
11	**2b**	K_2CO_3	MeOH	86 : 14	60 : 40
12[g]	**2c**	DBU	^{i}PrOH	47 : 53[h]	81 : 19

[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b] Determined by the ^{1}H NMR analysis of the reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** in all entries. [c] Determined by HPLC analysis. [d] TMG = 1,1,3,3-tetramethylguanidine. [e] **3b** was isolated in 86% yield. [f] A small amount of isopropyl ester was formed. [g] For 48 h. [h] **3c** and **4c** were isolated in 33% and 46% yield, respectively.

Table 2 Hydrogenation of methoxyquinolines[a]



Entry	2	Solvent	Temp./°C	3 : 3′ : 4[b]	Yield[c]/%	Er (3)[d]
1	**2d**	^{i}PrOH	80	100 : 0 : 0	91	—
2	**2e**	^{i}PrOH	80	100 : 0 : 0	99	—
3	**2f**	^{i}PrOH	80	52 : 40 : 8	40	71 : 29
4	**2g**	^{i}PrOH	80	75 : 0 : 25	79	79 : 21
5	**2h**	^{i}PrOH	80	86 : 0 : 14	84	68 : 32
6	**2i**	^{i}PrOH	80	86 : 14 : 0	79	90 : 10
7	**2i**	EtOAc	80	100 : 0 : 0	90	91 : 9
8	**2i**	EtOAc	60	100 : 0 : 0	80	91 : 9
9[e]	**2i**	EtOAc	60	100 : 0 : 0	94	91 : 9
10[f]	**2j**	EtOAc	60	0 : 0 : 24	—	—

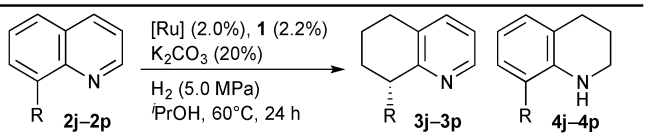
[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b] Determined by the ^{1}H NMR analysis of the reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** unless otherwise noted. [c] Isolated yields. [d] Determined by HPLC analysis. [e] With 0.5% catalyst loading. [f] 24% conversion.

give 1,2,3,4-tetrahydroquinoline **4b** as the major product. A small amount of 5,6,7,8-tetrahydroquinoline **3b** was obtained from the reaction. The enantiomeric ratio of **3b** was only 66 : 34. The molar ratio of **3b** to **4b** and the enantiopurity of **3b** scarcely varied in the absence of Et_3N (entry 2). These results suggest that the trialkylamine might be insufficient in basicity for the desired chemoselective hydrogenation. Various bases were evaluated for the reaction of **2b** (entries 3–6). The use of a guanidine or amidine base, which is more basic than Et_3N,[15] facilitated the hydrogenation of the carbocycle (entries 3 and 4). The chemoselectivity was reversed when DBU was used in place of Et_3N. Furthermore, alkali metal carbonates were favorable for the desired hydrogenation (entries 5 and 6). The percentage of **3b** increased with the increasing polarity of solvent (entries 7–11). The *trans*-chelating properties of **1**[6a] may be crucial for the selective reduction of the carbocyclic arenes. The pyridine ring of **2b** was selectively reduced when the hydrogenation was conducted with common bidentate bisphosphines, which chelate to a transition-metal in a *cis* manner.[16] In contrast to the chemoselectivity, the stereoselectivity was scarcely affected by the base additive and the solvent. The enantiomeric ratio of the hydrogenation product remarkably increased when 6-alkylquinoline **2c** was used as the substrate, but the molar ratio of **3c** to **4c** was *ca.* 1 : 1 (entry 12). The isopropyl group of **2c** may sterically obstruct the interaction between the catalyst and the carbocycle.

To investigate the effect of the position of the substituent on the quinoline core, we conducted the hydrogenation reactions of a series of methoxyquinolines in 2-propanol with the **1**–ruthenium catalyst (Table 2). Quinolines **2d** and **2e**, which have a methoxy group on the pyridine ring, were exclusively converted to achiral **3d** and **3e**, respectively (entries 1 and 2). Also 5,6,7,8-tetrahydroquinolines **3f–3h** are preferentially formed in the hydrogenations of **2f–2h**, which have a methoxy group on the carbocyclic ring (entries 3–5). The reactions, however, were accompanied by the formation of 1,2,3,4-tetrahydroquinoline **4**. The substituent on the 5-, 6-, or 7-position might somewhat hinder the formation of **3**. The enantiomeric ratios of **3f–3h** were moderate. Meanwhile, the hydrogenation of 8-methoxyquinoline (**2i**) took place on its carbocycle without the reduction of its heterocycle (entry 6). The position of the methoxy group affected the enantioselectivity as well as the chemoselectivity. Hydrogenation product **3i** was obtained with a higher enantiomeric ratio than **3f–3h**. The ruthenium catalyst cleaved the benzylic C–O bond to form **3′** in 2-propanol. The undesired hydrogenolysis was completely suppressed by conducting the reaction in an aprotic solvent, such as ethyl acetate (entry 7). Furthermore, the enantioselectivity was scarcely affected by the reaction temperature (entry 8). The catalyst loading can be reduced to 0.5% without loss of enantioselectivity (entry 9). The chemoselectivity completely inverted in the hydrogenation of 7,8-disubstituted quinoline **2j**, which exclusively gave the achiral 1,2,3,4-tetrahydroquinoline **4j** in low yield (entry 10).

As shown in Table 3, the **1**–ruthenium catalyst converted various 8-substituted quinolines to the corresponding chiral 5,6,7,8-tetrahydroquinolines with good enantiomeric ratios. As with methoxyquinoline **2i**, protected 8-hydroxyquinoline **2j** was hydrogenated to **3j** with 90 : 10 er in high yield (entry 1). The reduction of the aryl-substituted quinolines **2k–2m** also selectively took place on their carbocycles to give the desired chiral products **3k–3m** with 86 : 14 er (entries 2–4). The enantiomeric ratio was scarcely affected by the electronic properties of the

Table 3 Hydrogenation of 8-substituted quinolines[a]

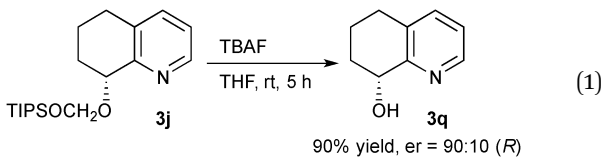


Entry	R (2)	3 : 4[b]	Yield[c]/%	Er (3)[d]
1[e]	$TIPSOCH_2O$ (**2j**)	100 : 0	97	90 : 10
2[f]	Ph (**2k**)	96 : 4	87	86 : 14
3	4-$MeOC_6H_4$ (**2l**)	100 : 0	94	86 : 14
4	4-$CF_3C_6H_4$ (**2m**)	100 : 0	88	86 : 14
5	2-MeC_6H_4 (**2n**)	71 : 29	56	70 : 30
6	Me (**2o**)	96 : 4[g]	75	88 : 12
7[h]	Me (**2o**)	94 : 6[g]	71	89 : 11
8[h]	[c]Hex (**2p**)	94 : 6	86	91 : 9

[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b] Determined by the ^{1}H NMR analysis of the reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** in all entries. [c] Isolated yields. [d] Determined by HPLC analysis. [e] In EtOAc. [f] At 40 °C for 48 h. [g] Determined by the GC analysis of the reaction mixture. [h] [RuCl(*p*-cymene) (**1**)]Cl and DBU were used in place of Ru(η^3-methallyl)$_2$(cod)–**1** and K_2CO_3, respectively.

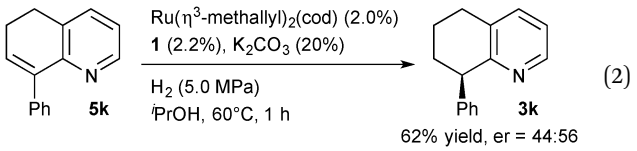
para-substituent in **2l** or **2m**. The *ortho*-substituent of **2n** disturbed the stereoselectivity as well as the chemoselectivity (entry 5). For the hydrogenation of 8-alkylquinolines, [RuCl(*p*-cymene) (**1**)]Cl, exhibited higher enantioselectivity than the *in situ*-generated Ru(η^3-methallyl)$_2$(cod)–**1** catalyst (entries 6 and 7). The preformed catalyst transformed **2o** and **2p** into **3o** and **3p** with 89 : 11 and 91 : 9 er, respectively (entries 7 and 8).

Hydrogenation product **3j** was treated with TBAF to give 8-hydroxy-5,6,7,8-tetrahydroquinoline **3q** with little loss of the enantiopurity (eqn (1)).[17] The optically active alcohol **3q** is useful as a chiral building block for preparing chiral catalysts[18] or various 8-substituted tetrahydroquinolines.[19] The absolute configuration of **3q** was assigned to be *R* with the sign of its optical rotation.



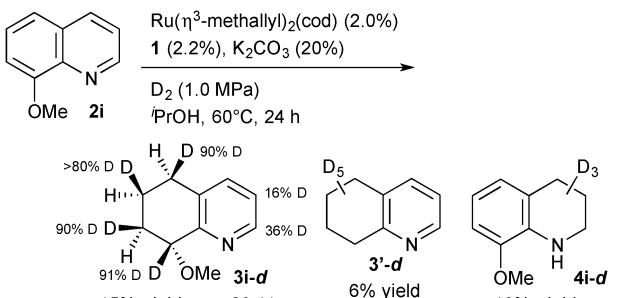
(1)

As shown in Scheme 2, three pathways can be speculated for the present ruthenium-catalyzed hydrogenation of quinoline carbocycles. In path A, the C5–C6 double bond is first saturated with H_2 to dearomatize the carbocycle, and then the remaining C–C double bond in the resulting intermediate **5** is enantioselectively hydrogenated with the chiral ruthenium catalyst to give the optically active product **3**. Path B or C starts from the hydrogenation of the C7–C8 double bond or the 1,4-addition of H_2 to the C5–C8 1,3-diene moiety, respectively. In these pathways, the dearomatization of the carbocycle is accompanied by the chiral induction. To confirm the possibility of path A, the hydrogenation of 5,6-dihydroquinoline **5k** was carried out under the optimized conditions for the asymmetric hydrogenation of **2** (eqn (2)). Hydrogenation product **3k** was obtained with a low enantiomeric ratio. The observed stereoselectivity rules out path A.



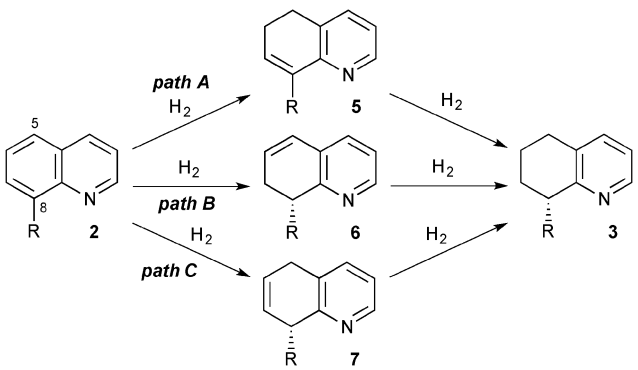
(2)

To further investigate the pathway of the hydrogenation, the deuterations of **2i** and **2k** were carried out with the **1**–ruthenium catalyst. The use of D_2 induced the reduction of the pyridine ring as well as significantly decreased the reaction rate.[16] Although D_2 scarcely reacted with **2k**, substrate **2i** was deuterated to give **3i-*d*** in 15% yield (by ^{1}H NMR) (eqn (3)). The deuteration of **2i** was accompanied by the formation of **3′-*d*** and **4i-*d***. In **3i-*d***, four deuterium atoms were incorporated at each of the 5-, 6-, 7-, and 8-positions with all *cis* stereochemistry. The stereochemistry may also rule out path A if the initial step does not proceed with a high degree of enantioface discrimination. Furthermore, the observed deuterium distribution suggests that the present hydrogenation of quinoline carbocycles involves no migration of the C–C double bond in dihydroquinoline intermediate **6** or **7**.



(3)

In conclusion, the PhTRAP–ruthenium complex allows the hydrogenation of quinolines **2** to selectively produce 5,6,7,8-tetrahydroqunolines **3**. The unusual chemoselectivity may be caused by the *trans*-chelating properties of the chiral ligand. Various 8-substituted quinolines were converted to the corresponding products **3** with good enantiomeric ratios (up to 91 : 9). Additionally, some experimental results suggested that the aromaticity-breaking step is accompanied by the chiral induction in the present asymmetric hydrogenation of quinoline



Scheme 2 Three possible pathways for the hydrogenation of quinoline carbocycles.

carbocycles, while the chiral induction took place in the reduction of the alkenyl ether intermediate in the asymmetric hydrogenation of naphthalenes reported by us.[5] Further mechanistic studies are in progress.

This work was partly supported by ACT-C (JST). We thank the Cooperative Research Program of ''Network Joint Research Center for Material and Devices'' for HRMS measurements.

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