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EDGE ARTICLE

Dehydration triggered asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles†

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Highly enantioselective hydrogenation of 3-(α-hydroxyalkyl)indoles promoted by a Brønsted acid for dehydration to form a vinylogous iminium intermediate *in situ* was developed with $Pd(OCOCF_3)_2$/(*R*)-H8-BINAP as catalyst with up to 97% ee. This methodology provides an efficient and rapid access to chiral 2,3-disubstituted indolines.

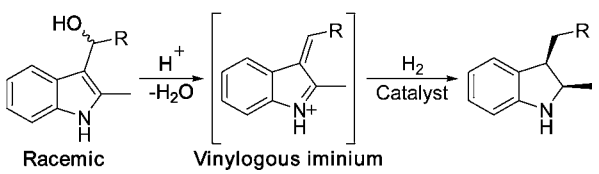
Catalytic asymmetric hydrogenation of prochiral compounds, such as olefins, ketones and imines, is one of the well-established reactions and holds a venerable position in organic synthesis.[1] Nevertheless, the asymmetric hydrogenation of aromatic and heteroaromatic compounds had been unexplored until recently.[2] This may mainly ascribe to the high stability of these compounds and harsh conditions needed to destroy the aromaticity which adversely affects the enantioselectivity.[3] Consequently, activation strategies for both catalyst and substrate emerged as the solution for the successful asymmetric hydrogenation of aromatic compounds. Based on this principle, some transition-metal and organic catalysts have been successfully introduced to the asymmetric hydrogenation[2] and transfer hydrogenation[4] of heteroaromatic compounds. Heretofore, some breakthroughs have been achieved in the asymmetric reduction of heteroaromatic compounds such as quinolines, quinoxalines, pyridines, indoles, pyrroles and furans.[5,6] Despite advances, it was far from meeting the continuously expansive requirement of the corresponding chiral saturated compounds in pharmaceutical and agrochemical synthesis.[7] Some heteroaromatic compounds even have been eluded for asymmetric hydrogenation.

In 2003, our group reported the first asymmetric hydrogenation of quinolines employing iodine as an additive to activate the iridium catalysts.[8a] Thereafter, this strategy was extensively employed in the hydrogenation of quinolines as well as pyridines[8c] and quinoxalines by us and others. Then, chloroformate was applied as substrate activator for asymmetric hydrogenation of quinolines as well as isoquinolines by us.[8b] Very recently, we described the asymmetric hydrogenation of quinolines and simple indoles with catalytic and stoichiometric amount of Brønsted acid as activator, respectively.[8d,9] In our ongoing efforts toward the development of asymmetric hydrogenation of aromatic compounds, we became interested in exploring new substrate activation strategies.

Easily available 3-(α-hydroxyalkyl)indoles can readily dehydrate to form vinylogous iminium intermediates *in situ* in the presence of Brønsted acids, which have been successfully applied to some chemical transformations.[10] We envision that the active vinylogous iminium intermediate should be easily hydrogenated with a proper catalytic system since the aromaticity has been partially destroyed. This partial dearomatization process triggered by dehydration offered a new opportunity to the asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles (Scheme 1). In this communication, asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles is successfully developed with up to 97% ee.

A series of racemic 2,3-disubstituted 3-(α-hydroxyalkyl)indoles was synthesized rapidly and conveniently through a divergent approach starting from the formylation of 2-substituted indoles followed by nucleophilic additions with various Grignard Reagents.[10h,11]

Obviously, both acid and water were existing in this system, and accordingly the asymmetric hydrogenation catalysts must be compatible with both acid and water. Recently, chiral palladium catalysts have been successfully applied to asymmetric hydrogenation of activated imines, simple indoles and functionalized ketones by us and other groups.[9,12] Our preliminary mechanistic



Scheme 1 Dehydration triggered partial dearomatization of 3-(α-hydroxyalkyl)indoles for hydrogenation.

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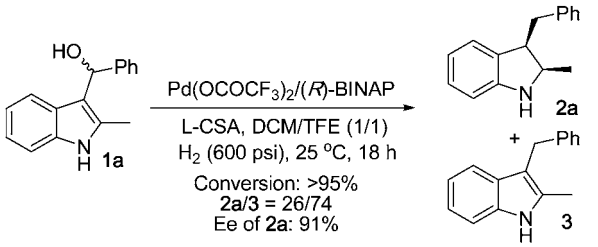
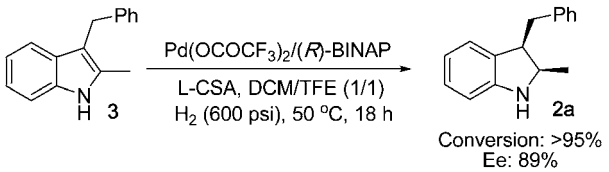
study found the chiral palladium catalyst is not sensitive to acid and water. Therefore, chiral palladium catalysts should be a good choice for the asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles.

Initially, (2-methyl-*1H*-indol-3-yl)(phenyl)methanol **1a** was selected as a model substrate to test our hypothesis. Pd$(OCOCF_3)_2$/(*R*)-BINAP was employed as catalyst and L-camphorsulfonic acid (L-CSA) as the activator, the hydrogenation reaction was conducted in a mixture of solvents DCM/TFE (dichloromethane and 2,2,2-trifluoroethanol: 1/1) at 50 °C.[9] The reaction proceeded smoothly to give the desired product **2a** with 86% yield and 86% ee (Table 1, entry 1). Catalytic amount of activator was tested but with low yield and decreased ee (entry 2). Mixed solvents of DCM and TFE with different ratios were examined (entries 3–6), and the best result was obtained with the ratio of 2/1 in terms of enantioselectivity (entry 3, 88% ee). Next, the effect of different acid activators on the reactivity and enantioselectivity was examined (entries 7–10). It was found that strong Brønsted acid was necessary for obtaining the desired product **2a** (entries 7–9). When weak acid, benzoic acid, was applied in this transformation, no desirable product was obtained (entry 10). Commercially available *p*-toluenesulfonic acid monohydrate ($TsOH\cdot H_2O$) gave both high yield and enantioselectivity, and it was selected for further studies (entry 7, 87% ee). Ligand screen indicated that (*R*)-H8-BINAP gave the highest enantioselectivity (entry 11, 91% ee). Therefore, the optimal conditions were established as the following: Pd$(OCOCF_3)_2$/(*R*)-H8-BINAP/$TsOH\cdot H_2O$/H_2 (600 psi)/DCM-TFE (2 : 1)/50 °C.

Various 3-(α-hydroxyalkyl)indoles were subjected to the Pd-catalyzed asymmetric hydrogenation as shown in Table 2. For 2-methyl substituted substrates **1a–1h**, when R^3 is an aryl group, excellent enantioselectivities (88–91% ee) were obtained regardless of position and electronic effect of substituents of phenyl ring (entries 1–6). When R^3 is an alkyl group, slightly higher enantioselectivities were obtained (entries 7–8). For 2-butyl and 2-phenethyl substituted indoles **1i–1l**, 93–96% ee were obtained (entries 9–12). Substitution at the 5-position gave negative effect on enantioselectivity which may ascribe to both steric and electronic effect (entries 13–14). Excellent 94–97% ee were achieved with substrates assembled with a methyl substituent at 7-position (entries 15–20), and this may ascribe to the steric effect of 7-methyl.



(1)

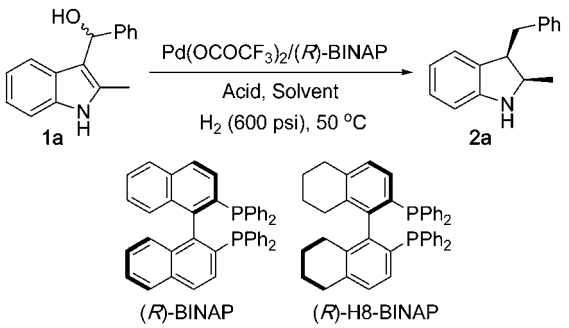


(2)

The hydrogenation reaction was driven by Brønsted acid promoting dehydration to form a vinylogous iminium *in situ*. To obtain information on the hydrogenation reaction of vinylogous iminium intermediate, we performed hydrogenation reaction of 3-(α-hydroxyalkyl)indole **1a** at room temperature using the chiral palladium complex as catalyst (eqn (1)). The desirable product **2a** was obtained with 91% ee, and indole **3** was the main product (**2a/3** = 26/74). When **3** was subjected to hydrogenation at 50 °C (eqn (2)), full conversion and 89% ee were obtained. These results indicated that indole **3** might be the intermediate for the 3-(α-hydroxyalkyl)indole hydrogenation.[9]

By analysis of Pd-catalyzed hydrogenation sequence of C=C and C=N bonds of vinylogous iminium intermediate, we envisioned that there might be three possible paths.[13] Path A: 1,2-hydride addition and isomerization to form indole, and then acid activated indole hydrogenation. Path B: 3,4-hydride addition and isomerization to form indole, as well as acid activated indole hydrogenation. Path C: 1,4-hydride addition to form indole followed by acid activated indole hydrogenation. To shed light on the reaction mechanism, we performed three isotopic labeling experiments with deuterated solvent and deuterium gas, respectively (Scheme 2).[13] When the hydrogenation was carried out in deuterated TFE for 18.5 h, full conversion was attained with **2a** as the product. One deuterium atom was detected at the

Table 1 Optimization for asymmetric hydrogenation of **1a**.

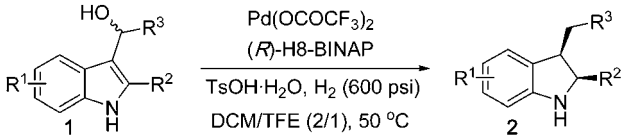


[a]

Entry	Solvent	Acid	Yield (%)	ee (%)[b]
1	DCM/TFE (1/1)	L-CSA	86	86
2[c]	DCM/TFE (1/1)	L-CSA	20[d]	71
3	DCM/TFE (2/1)	L-CSA	75	88
4	DCM	L-CSA	58[d]	57
5	DCM/TFE (1/2)	L-CSA	79	79
6	TFE	L-CSA	68	86
7	DCM/TFE (2/1)	$TsOH\cdot H_2O$	91	87
8	DCM/TFE (2/1)	TfOH	97	77
9	DCM/TFE (2/1)	TFA	81	43
10	DCM/TFE (2/1)	$PhCO_2H$	—[d]	—
11[e]	DCM/TFE (2/1)	$TsOH\cdot H_2O$	96	91
12	DCM/TFE (2/1)	D-CSA	74	78

[a] Conditions: 0.25 mmol **1a**, Pd$(OCOCF_3)_2$ (2 mol%), (*R*)-BINAP (2.4 mol%), acid (0.25 mmol), 3 mL solvent, 50 °C, 16–24 h. [b] Determined by HPLC. [c] With 0.05 mmol L-CSA (0.2 equiv). [d] With full conversion of **1a** and 2-methyl-3-benzylindole **3** was obtained as byproduct. [e] With (*R*)-H8-BINAP as ligand.

Table 2 Asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles **1**.



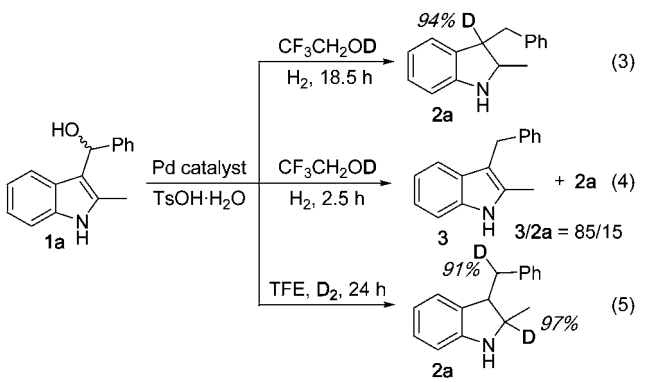
[a]

Entry	R^1	R^2	R^3	Yield (%)	ee (%)[b]
1	H	Me	Ph	96 (**2a**)	91
2	H	Me	4-MeC_6H_4	97 (**2b**)	90
3	H	Me	3-MeC_6H_4	86 (**2c**)	90
4	H	Me	2-MeC_6H_4	85 (**2d**)	91
5	H	Me	4-$MeOC_6H_4$	86 (**2e**)	89
6	H	Me	4-FC_6H_4	88 (**2f**)	88
7	H	Me	Cy	95 (**2g**)	94
8	H	Me	*i*-Pr	99 (**2h**)	94
9	H	*n*-Bu	Ph	94 (**2i**)	94
10	H	*n*-Bu	Cy	96 (**2j**)	96
11	H	Phenethyl	Ph	85 (**2k**)	93
12	H	Phenethyl	Cy	78 (**2l**)	95
13	5-F	Me	Ph	92 (**2m**)	85
14	5-F	Me	Cy	91 (**2n**)	88
15	7-Me	Me	Ph	84 (**2o**)	97
16	7-Me	Me	4-MeC_6H_4	94 (**2p**)	96
17	7-Me	Me	3-MeC_6H_4	92 (**2q**)	95
18	7-Me	Me	2-MeC_6H_4	99 (**2r**)	94
19	7-Me	Me	Cy	98 (**2s**)	97
20	7-Me	Me	*i*-Pr	98 (**2t**)	97

[a] Conditions: 0.25 mmol **1**, $Pd(OCOCF_3)_2$ (2 mol%), (*R*)-H8-BINAP (2.4 mol%), $TsOH \cdot H_2O$ (0.25 mmol), 3 mL solvent, 50 °C, 16–24 h. [b] Determined by HPLC.

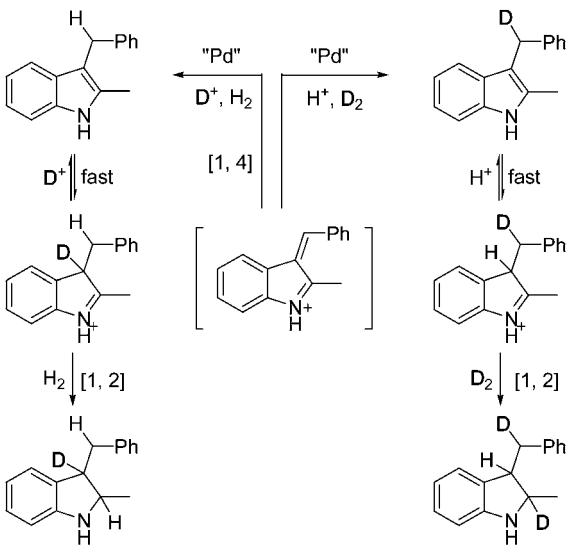
3-position with 94% incorporation (eqn 3). When the hydrogenation reaction was stopped at 2.5 h, **3** and **2a** were obtained at a ratio of 85/15; ^1H NMR analysis of the isolated indole **3** showed no deuterium atom was incorporated at the benzylic position (eqn 4). When **1a** was treated with D_2, **2a** was obtained with 97% and 91% incorporation of deuterium at 2- and benzylic position, respectively (eqn 5).

With path A, when deuterium gas is used, only one deuterium atom should be incorporated to the 2 position of indoline **2**. The incorporation of two deuterium atoms in the product excludes this path (Scheme 2, eqn 5). For the paths B and C, isotopic labeling experiments cannot completely differentiate. Path C is more favorable in thermodynamics than path B because of rapid recovery of aromatization. Hence, the hydrogenation sequence



Scheme 2 Deuterium-labeling studies.

of the C=C and C=N bonds of the iminium intermediate could be determined as 1,4-hydride addition followed by 1,2-hydride addition (Scheme 3). The first hydrogen molecule could be readily added to the vinylogous iminium through 1,4-hydride addition to form 2,3-disubstituted indole and thus recovered its aromaticity. The further hydrogenation of the indole must be activated by strong Brønsted acid to form an iminium



Scheme 3 Proposed process of 3-(α-hydroxyalkyl)indoles hydrogenation.

intermediate, which was hydrogenated *via* 1,2-hydride addition as disclosed in our previous work.[9]

In summary, we have developed an efficient activation strategy for the Pd-catalyzed asymmetric hydrogenation of 3-(α-hydroxyalkyl)indoles with a Brønsted acid as an activator. Dehydration is the driving force for the reductive removal of the hydroxy group with the formation of vinylogous iminium intermediate. The starting racemic 3-(α-hydroxyalkyl)indoles are readily accessible and this methodology provides an efficient and rapid access to the chiral 2,3-disubstituted indolines.

Acknowledgements

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13 For detailed information about the study of mechanism, see the Supporting Information.

