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Formal Palladium-Catalyzed Asymmetric Hydrogenolysis of Racemic *N*-Sulfonyloxaziridines

Bo Song, Chang-Bin Yu, Wen-Xue Huang, Mu-Wang Chen, and Yong-Gui Zhou*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Supporting Information

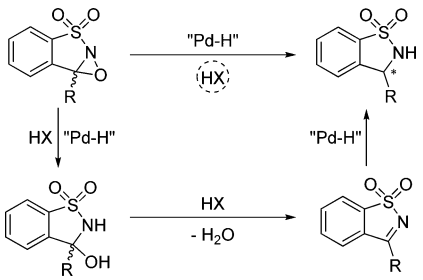
ABSTRACT: Highly enantioselective palladium-catalyzed formal hydrogenolysis of racemic *N*-sulfonyloxaziridines has been realized, providing a novel access to sultams with up to 99% ee. Preliminary mechanistic insights revealed that the reaction proceeded through a N−O bond cleavage, dehydration, and the sequential asymmetric hydrogenation.

Hydrogenolysis is a powerful method with extensive use in industrial applications, pharmaceutical synthesis, and organic synthesis.[1] While the hydrogenolysis reaction is widely employed to synthesize racemic or achiral compounds, very few asymmetric versions have been developed to date. Initial efforts for asymmetric hydrogenolysis focused on the development of desymmetrization of epoxides[2] and *meso* dihalide complexes.[3] Recently, asymmetric hydrogenolysis of racemic tertiary alcohols has also been achieved with high optical enrichment.[4] Owing to the variability and fragility of compounds in hydrogenolysis conditions, the synthetic utility of hydrogenolysis is difficult to conduct in asymmetric form. Therefore, the enlargement of the range of substrates poses a key challenge for the development of asymmetric hydrogenolysis reactions.

Soon after their first preparation by Emmons in 1957,[5] oxaziridines[6] became regarded as fascinating objectives for novel and unusual chemistry and were utilized in oxygen or nitrogen atom transfer reactions, rearrangements, and cycloadditions. *N*-sulfonyloxaziridines, commonly referred to as "Davis' oxaziridines",[7] were the most extensively utilized class of oxaziridines in organic synthesis attributing to their stability, ready availability, and superior reactivity.[6j] Facilitated by ring strain releasing, a ring opening reaction easily occurs to the strained three-membered heterocyclic compounds containing two adjacent electronegative heteroatoms. The experimental and theoretical mechanistic investigations corroborate that the oxygen transfer reaction of the oxaziridines is usually deemed to be a concerted process with simultaneous disconnection of N−O and C−O bonds.[8] Furthermore, an alternative transition-state model, in which the N−O bond cleaves ahead of a C−O bond, is also proposed by Evans, Davis, and Dmitrienko.[9]

Very recently, we reported a Pd-catalyzed asymmetric hydrogenolysis of *N*-sulfonyl aminoalcohols.[4d] Mechanism studies indicated that *N*-sulfonyl aminoalcohols were dehydrated in the presence of trifluoroacetic acid to afford achiral enesulfonamide intermediates, followed by asymmetric hydrogenation to provide the desired products. Taking the convenient synthesis of *N*-sulfonyl oxaziridines from commercially available starting marterials[10] and ready cleavage of a C−O or N−O bond into consideration, we cogitated if *N*-sulfonyloxaziridines could be controlled to disconnect the N−O bond and then transformed to imines with the aid of Brønsted acids, which have been successfully applied in homogeneous Pd-catalyzed asymmetric hydrogenation (Scheme 1).[11] Herein, we document the enantioselective synthesis of sultams by a Pd-catalyzed formal hydrogenolysis of racemic *N*-sulfonyloxaziridines with up to 99% ee.

Scheme 1. Asymmetric Hydrogenolysis of *N*-Sulfonyloxaziridines



We began our investigation with 3-phenyl-1,2-benzisothiazole 1,1-dioxide oxide **1a** as the model substrate using the $Pd(OCOCF_3)_2$/(*S*,*S*′,*R*,*R*′)-TangPhos complex as the catalyst. To our delight, the desired sultam **2a** was obtained in moderate yield and excellent enantioselectivity employing catalytic amounts of benzoic acid as an additive (Table 1, entry 1). The activity of this protocol can be improved by changing Brønsted acids. With di-*p*-toluoyl-D-tartaric acid (D-DTTA), a higher yield but with a somewhat lower ee value was obtained (entry 2). Several other acids were then examined. Of the acid additives, L-camphorsulfonic acid (L-CSA) afforded both an excellent yield and ee value, resembling D-camphorsulfonic acid (D-CSA) which gave a slightly lower enantioseletivity (entries 3−5). The choice

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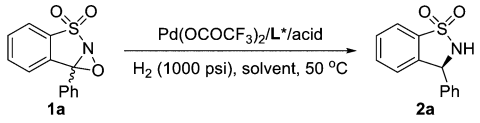
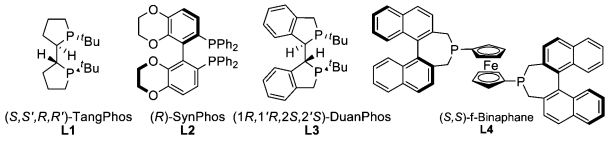
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	ligand	acid	yield (%)[b]	ee (%)[c]
1	DCM	**L1**	PhCOOH	53	96
2	DCM	**L1**	D-DTTA	63	93
3	DCM	**L1**	$TsOH·H_2O$	92	94
4	DCM	**L1**	D-CSA	95	96
5	DCM	**L1**	L-CSA	96	98
6	PhMe	**L1**	L-CSA	97	96
7	THF	**L1**	L-CSA	91	91
8	TFE	**L1**	L-CSA	28	93
9	DCM	**L2**	L-CSA	97	84
10	DCM	**L3**	L-CSA	75	90
11	DCM	**L4**	L-CSA	<5	N/A[g]
12[d]	DCM	**L1**	L-CSA	97	96
13[d,e]	DCM	**L1**	L-CSA	98	97
14[d,e,f]	DCM	**L1**	L-CSA	97	97

[a]Conditions: Oxaziridine **1a** (0.20 mmol), $Pd(OCOCF_3)_2$ (5.0 mol %), (*S*,*S*′,*R*,*R*′)-TangPhos (5.5 mol %), acid (10.0 mol %), H_2 (1000 psi), solvent (3.0 mL), 50 °C, 20 h. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. [c]Determined by HPLC. [d]The amount of catalyst is 3.0 mol %. [e]600 psi. [f]30 °C. [g]N/A: Not analyzed.

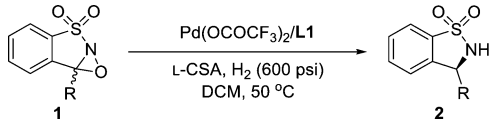


of solvents was also found to have a dramatic influence on the reaction activities while maintaining the prominent enantioselectivities, with DCM proving to be optimal (entries 6−8). Toluene was not endowed with good solubility for the catalyst, notwithstanding it provided a similar remarkable result. Next, we tested the performance of some other commercially available bisphosphine ligands. It turns out that no ligand gave better results other than (*S*,*S*′,*R*,*R*′)-TangPhos (entries 9−11). Fortunately, decreasing the amount of catalyst, reducing the pressure of hydrogen gas, and lowing the temperature failed to bring about deterioration in yields and enantioselectivities (entries 12−14).

With the optimized reaction conditions established, the scope of this transformation was subsequently investigated. As shown in Table 2, a range of 3-substituted-1,2-benzisothiazole 1,1-dioxide oxides **1** were found to be competent substrates. Not only alkyl but also aryl substituted substrates could be converted to products with excellent reactivities and enantioselectivities. It is of note that slightly higher ee values were obtained for aryl substituents than alkyl substituents of *N*-sulfonyloxaziridines, which may be ascribed to the distinct electronic properties. Especially, the sterically hindered 2-methyl and 2-methoxy group on the phenyl ring for the substrates **1b** and **1f**, respectively, culminated in the best enantioselectivities (entries 2 and 6).

To further determine the substrate generality of this protocol, multifarious nonbenzofused *N*-sulfonyloxaziridines were also subjected to the modified optimal conditions, and the results are summarized in Table 3. To our satisfaction, various oxaziridines **3** can serve as efficacious substrates. With respect to aryl-substituted substrates, the impact that steric effect had on

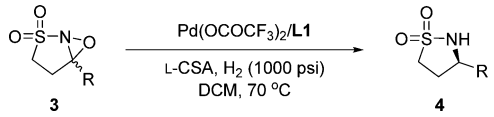
Table 2. Substrate Scopes[a]



entry	R	yield (%)[b]	ee (%)[c]
1[d]	C_6H_5	97 (**2a**)	97 (*S*)
2[e]	2-MeC_6H_4	96 (**2b**)	99 (*S*)
3[d]	3-MeC_6H_4	97 (**2c**)	96 (*S*)
4	4-MeC_6H_4	94 (**2d**)	98 (*S*)
5	4-FC_6H_4	96 (**2e**)	97 (*S*)
6	2-$MeOC_6H_4$	98 (**2f**)	98 (*S*)
7	3,5-$(MeO)_2C_6H_3$	96 (**2g**)	97 (*S*)
8	Me	98 (**2h**)	93 (*S*)
9	^{n}Bu	95 (**2i**)	94 (*S*)
10	^{i}Bu	96 (**2j**)	97 (*S*)
11[e]	Cy	94 (**2k**)	97 (*S*)
12	$C_6H_5CH_2CH_2$	97 (**2l**)	95 (*S*)

[a]Conditions: Oxaziridine **1** (0.20 mmol), $Pd(OCOCF_3)_2$ (3.0 mol %), (*S*,*S*′,*R*,*R*′)-TangPhos (3.3 mol %), L-CSA (10.0 mol %), H_2 (600 psi), DCM (3.0 mL), 50 °C, 20 h. [b]Isolated yields. [c]Determined by HPLC. [d]30 °C. [e]1000 psi.

Table 3. Substrate Scopes[a]



entry	R	yield (%)[b]	ee (%)[c]
1	C_6H_5	87 (**4a**)	91 (*R*)
2	2-MeC_6H_4	93 (**4b**)	97 (*R*)
3	3-MeC_6H_4	90 (**4c**)	91 (*R*)
4	4-MeC_6H_4	80 (**4d**)	90 (*R*)
5	^{n}Bu	91 (**4e**)	98 (*S*)
6[d]	$C_6H_5OCH_2$	96 (**4f**)	94 (*R*)
7[d]	2-$MeC_6H_4OCH_2$	94 (**4g**)	94 (*R*)
8[d]	4-$MeC_6H_4OCH_2$	98 (**4h**)	94 (*R*)
9[d]	2-Naphthyl-OCH_2	93 (**4i**)	94 (*R*)

[a]Conditions: Oxaziridine **3** (0.20 mmol), $Pd(OCOCF_3)_2$ (5.0 mol %), (*S*,*S*′,*R*,*R*′)-TangPhos (5.5 mol %), L-CSA (10.0 mol %), H_2 (1000 psi), DCM (3.0 mL), 70 °C, 20 h. [b]Isolated yields. [c]Determined by HPLC. [d]The amount of catalyst is 3.0 mol %, 50 °C.

activities and enantioselectivities was moderate (entries 1−4). It is worthwhile to note that the hydrogenolysis of simple alkyl-substituted substrate **3e** proceeded smoothly and the expected good yield and high ee value were obtained (entry 5). Moreover, mild reaction conditions with a reduced catalyst loading and low temperature could be applied to an array of aryloxymethyl-substituted substrates, providing the chiral sultams **4** with excellent yields and enantioselectivities (entries 6−9).[12]

To obtain further insight into the reaction pathway, several control experiments were carried out, as summarized in Table 4. When the reaction was conducted under a reduced pressure of hydrogen gas for 1 h, dynamic kinetic resolution of *N*-sulfonyloxaziridines was not observed and racemic starting material **1a** was recovered.[13] In addition, 2-benzoylbenzene-sulfonamide **5** and imine **6a** were detected, illustrating that imine **6a** and 2-benzoylbenzenesulfonamide **5** might participate in this process (entry 1). If the reaction carried out only for 1 h was quenched, imine **6a** and 2-benzoylbenzene-sulfonamide **5** were

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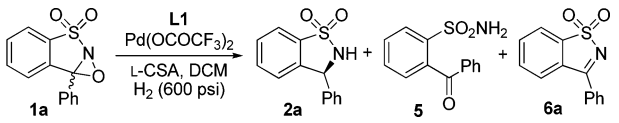
Table 4. Investigation of the Pathway for Asymmetric Hydrogenolysis of *N*-Sulfonyloxaziridines[a]



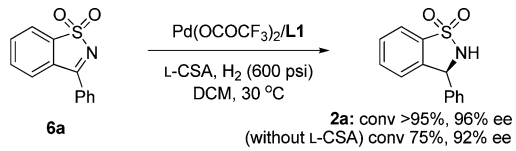
			selectivity (%)[b]			
entry	*t* (h)	conv (%)	**2a**	**5**	**6a**	ee of **2a** (%)[c]
1[d]	1	54	–[e]	30	70	N/A[f]
2	1	>95	27	32	41	96
3	5	>95	56	–[e]	44	97
4	10	>95	85	–[e]	15	96
5	15	>95	89	–[e]	11	96

[a]Conditions: Oxaziridine **1a** (0.20 mmol), $Pd(OCOCF_3)_2$ (3.0 mol %), (*S*,*S*′,*R*,*R*′)-TangPhos (3.3 mol %), L-CSA (10.0 mol %), H_2 (600 psi), DCM (3.0 mL), 30 °C. [b]Determined by ^1H NMR. [c]Determined by HPLC. [d]100 psi. [e]Not observed. [f]N/A: Not analyzed.

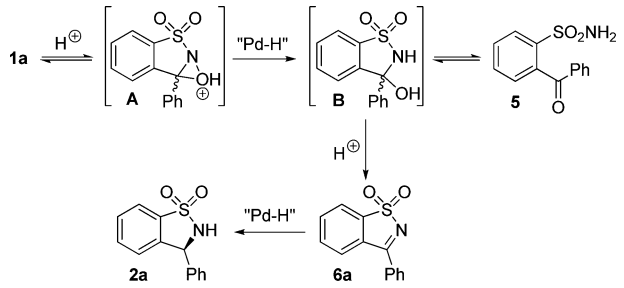
monitored besides sultam **2a** with almost the same ee value (entry 2). If reactions were conducted for more than 5 h, only the desired product and imine intermediate at various ratios were obtained (entries 3–5).

To obtain mechanistic information regarding the course of the hydrogenolysis, further control experiments were conducted. Intriguingly, imine **6** was submitted to the standard conditions furnishing the desired product **2a** with full conversion and an identical ee value, while the reaction conducted without L-CSA provided the desired product with 75% conversion and a lower ee value (Scheme 2). The mechanistic details of our proposed

Scheme 2. Mechanistic Investigation of the Asymmetric Hydrogenolysis of *N*-Sulfonyloxaziridines



Scheme 3. Plausible Reaction Pathway for the Asymmetric Hydrogenolysis of *N*-Sulfonyloxaziridines



stepwise formal hydrogenolysis process are outlined in Scheme 3 on the foundation of these experimental results and previous studies on the asymmetric hydrogenolysis of tertiary alcohols.[4] Reversible prontonation of oxaziridine **1a** rapidly produces **A**, which is readily transformed into tertiary alcohol **B** through disconnecting the N–O bond by hydrogenolysis. Thermodynamically unstable alcohol **B** can either reversibly isomerize into **5** or be easily dehydrated to *N*-sulfonylimine **6a**, which can be smoothly hydrogenated to desired product **2a**. L-CSA not only plays the part of acid for transformations but also acts as an activator for asymmetric hydrogenation.[14] It is worthwhile to mention that the transformation of **1a** to **B** and **B** to **6a** are faster than that of **6a** to **2a**.

In conclusion, we have developed the first homogeneous formal Pd-catalyzed asymmetric hydrogenolysis for a broad range of racemic aryl- and alkyl-substituted *N*-sulfonyloxaziridines, providing novel access to the chiral sultams with up to 99% ee. Explicit mechanism studies reveal that the reaction proceeds by a stepwise sequence initiated by the ring opening of *N*-sulfonyloxaziridine through hydrogenolysis, followed by a dehydration of the tertiary alcohol intermediate and then an asymmetric hydrogenation of the imine intermediate. Further work will be devoted to the synthetic application of the developed strategy.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ygzhou@dicp.ac.cn.

Notes

The authors declare no competing financial interest.

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(12) Acetophenone-derived *N*-sulfonyloxaziridines can also serve as the substrate for this catalytic system with an excellent ee value (93% ee), but only a 27% yield was obtained for the reason that acyclic acetophenone-derived *N*-sulfonylimine was ready to hydrolyze in the presence of acid (see Supporting Information).
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