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Rhodium-catalyzed intramolecular reductive aldol-type cyclization: Application for the synthesis of a chiral necic acid lactone

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Full Research Paper

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Abstract

A rhodium-catalyzed intramolecular reductive aldol-type cyclization is described to give β-hydroxylactones with high diastereoselectivities. The stereoselectivity of this cyclization is highly solvent dependent and can give *syn*- or *anti*-β-hydroxylactones with high diastereoselectivity. This methodology was also applied to the synthesis of a chiral necic acid lactone which is a structural component of the pyrrolizidine alkaloid monocrotaline.

Introduction

Carbon–carbon bond-forming reactions are among the most important reactions in the synthetic chemistry toolbox and the aldol reaction is one of the most powerful tools to achieve this transformation [1-8]. In particular, the intramolecular aldol condensation is an important approach to the formation of ring systems such as cyclic β-hydroxy carbonyl products or cyclic α,β-unsaturated carbonyl products. Therefore, various types of intramolecular aldol-type reactions have been developed and widely applied to the total synthesis of diverse natural products [9-18]. The reductive aldol-type reaction is another important variation that has been reported using metal catalysts such as Co [19-21], Cu [22-25], and others [26-32] with hydrosilanes (R_3Si-H) or hydrogen as the reductant. In this area, rhodium catalysis has received significant attention [33-40], and we have

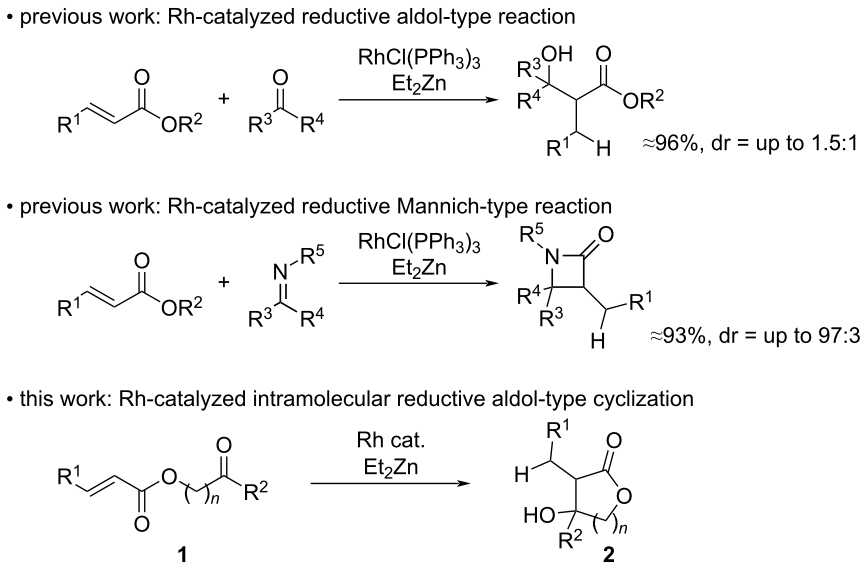
also reported reductive α-acylations, reductive aldol-type reactions, and reductive Mannich-type reactions using $RhCl(PPh_3)_3$ with Et_2Zn [41-47]. The rhodium-catalyzed reductive aldol reaction of α,β-unsaturated esters with aldehydes or ketones gives aldol-type products in good to excellent yields (Scheme 1) [43,44]. In addition, the reductive aldol-type reaction could also be applied to an asymmetric system, although the diastereoselectivity was poor. On the other hand, reductive Mannich-type reactions were achieved in good to excellent yields with high diastereoselectivity [45,46]. As part of a wider program of C–C bond formation systems, we herein report a rhodium-catalyzed intramolecular reductive aldol-type cyclization and its application for the synthesis of a chiral necic acid lactone.

Results and Discussion

Rh-catalyzed intramolecular cyclization

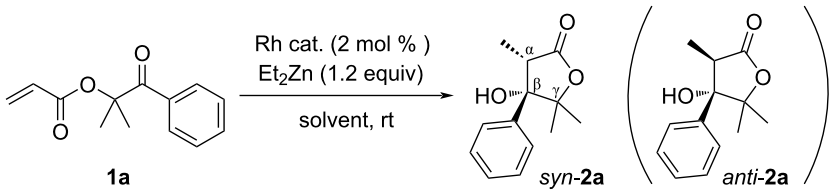
When applying our previously reported conditions [43], the intramolecular reductive aldol-type cyclization of **1a** proceeded smoothly and gave the desired product **2a** in a good yield, but the diastereomeric ratio was not sufficient as shown in entry 1 (Table 1). To improve the diastereoselectivity of the reaction, we optimized the conditions for the reductive aldol-type reaction by intramolecular cyclization of **1**, and the results are summarized in Table 1. The use of $[RhCl(cod)]_2$ in dichloromethane gave the best result with high diastereoselectivity, and the stereochemistry of the major product **2a** was found to be the *syn*-form with regard to the CH_3 (C^α) and OH (C^β) moieties (Table 1, entry 7). Interestingly, using the higher coordinating solvents, DMF or DMPU, preferentially gave the opposite diastereomer, i.e., the major product being the *anti*-form with regard to CH_3 (C^α) and OH (C^β) moieties (*anti*-**2a**, Table 1, entries 10 and 11). For stereochemistry assignment, the relative configurations of *syn*-**2a** and *anti*-**2a** were confirmed by X-ray crystallography. In addition, a NOESY experiment of the product *syn*-**2a** showed an nOe correlation between the methine proton on C^α and one of the protons of the benzene ring on C^β, but not in *anti*-**2a**.

Next, various substrates were investigated and the results are summarized in Scheme 2. The synthesis of products **2a**–**c** proceeded smoothly to give the corresponding β-hydroxylactones **2** in moderate to good yields with high diastereoselectivities, although **2d** was obtained in low yield. It may suggest that the existence of substituent(s) in γ- and/or δ-position of **2** help the formation of the intermediate structure which works in favor of the intramolecular cyclization. β-Substituted substrates on α,β-unsaturated ester moiety of **1** also gave the products (**2g** and **2h**) in low yields, but the formation of the 7-membered ring (**2f**) was not achieved. On the other hand, when the previous conditions using the $RhCl(PPh_3)_3$ catalyst was applied to the aldol-type cyclization, 5- and 6-membered products were obtained in good yields (see the yields and dr in parentheses in Scheme 2). However, the yields were also greatly affected by the substituents on the β-position of the α,β-unsaturated ester moiety, and all diastereomeric ratios were inferior in the case of the $RhCl(PPh_3)_3$ catalyst. The relative configurations of **2b** were confirmed by X-ray crystallography, and the relative configurations of **2c**, **2g**, and **2h** were confirmed by NOESY experiments.



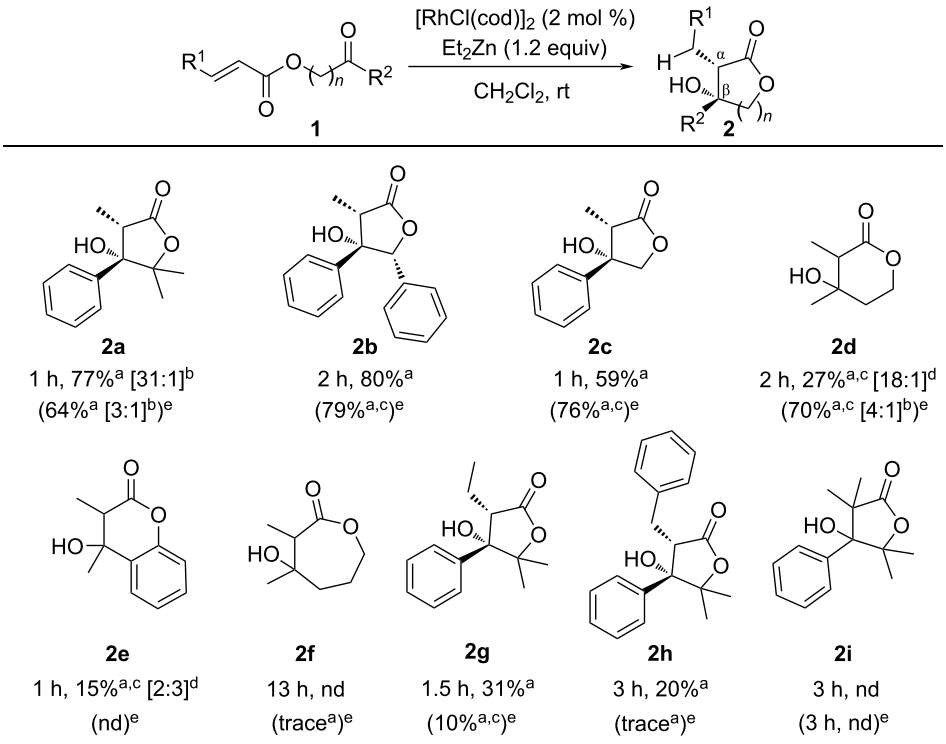
Scheme 1: Previous works and this work.

Table 1: Optimization of the reaction conditions.



Entry	Rh cat.	Solvent	Time (h)	Yield[a]	dr [*syn*:*anti*][b,c]
1	$RhCl(PPh_3)_3$	THF	1	64	[3:1]
2	$[RhCl(cod)]_2$	THF	1.5	72	[30:1]
3	$RhClCO(PPh_3)_2$	THF	1	85	[9:1]
4	$Rh(acac)(CO)_2$	THF	1	trace	–
5	$[RhCl(cod)]_2$	toluene	1	68	[14:1]
6	$[RhCl(cod)]_2$	AcOEt	1	79	[25:1]
7	$[RhCl(cod)]_2$	CH_2Cl_2	1	77	[31:1]
8	$[RhCl(cod)]_2$	DME	2	17[d]	–
9	$[RhCl(cod)]_2$	CH_3CN	1	71	[2:1]
10	$[RhCl(cod)]_2$	DMF	3	42	[1:27]
11	$[RhCl(cod)]_2$	DMPU	1	52	[1:50]

[a]Isolated yield; [b]the stereochemistry between CH_3 (C^{α}) and OH (C^{β}) moieties; [c]diastereomeric ratio was determined after purification; [d]diastereomeric mixture.



Scheme 2: Scope and limitation of the rhodium-catalyzed reductive aldol-type cyclization. [a]Isolated yield. [b]Diastereomeric ratio was determined after purification. [c]Diastereomeric mixture. [d]Diastereomeric ratio was determined by ^1H NMR. [e]The reaction was carried out using $RhCl(PPh_3)_3$ in THF at rt.

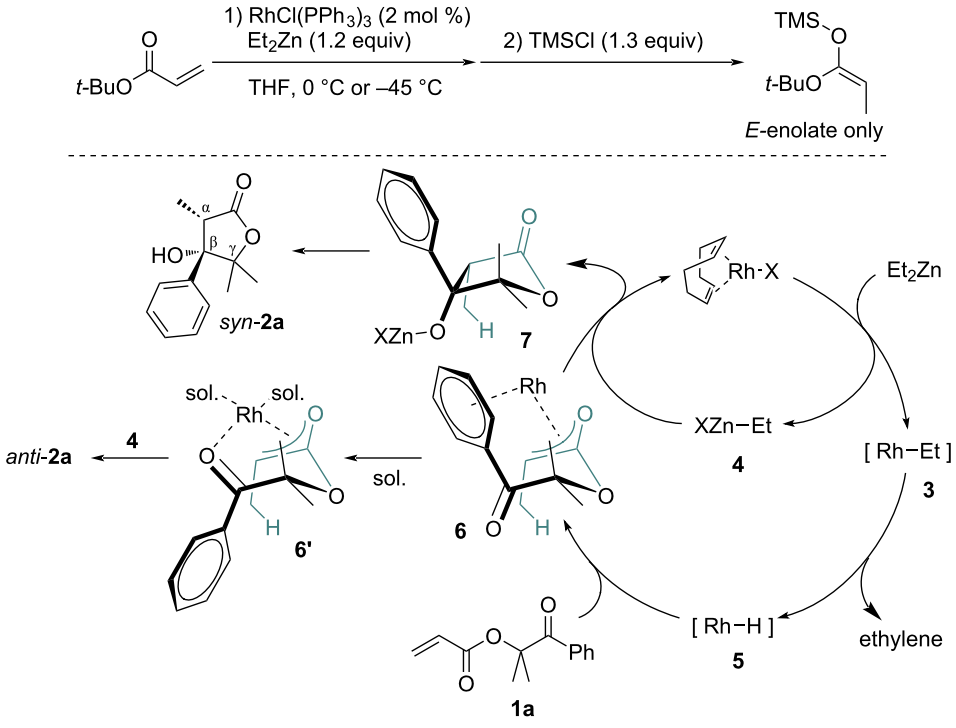
Mechanistic investigation of the intramolecular cyclization

The reaction mechanism of the intramolecular cyclization can only be speculative at this stage. We have already reported the generation of a rhodium hydride (Rh–H) complex from $RhCl(PPh_3)_3$ and Et_2Zn, in which the reaction with *tert*-butyl acrylate formed the corresponding *E*-silylenolate via 1,4-reduction at 0 °C [46], even if the reaction was performed at −45 °C (Scheme 3). Also in relation to this result, Mikami and his group reported a rhodium-catalyzed carboxylation of alkenes or activated alkenes by using CO_2 with Et_2Zn, and a similar Rh–H complex derived from $[RhCl(cod)]_2$ and Et_2Zn played an important role in this reaction [48]. Furthermore, Hopmann et al. detected the Rh–H complex derived from $[RhCl(cod)]_2$ and Et_2Zn by ^1H NMR, and the detailed mechanism disclosed that the Rh–H complex did not interact with CO_2 but with the benzene ring in the substrates through an η^6 binding intermediate by DFT calculation [49].

Although another mechanism could not be denied in which a *Z*-enolate intermediate changes to an *E*-enolate under thermodynamic control, we propose the following mechanism on the basis of the above results (Scheme 3). The Rh–H complex **5** from $[RhCl(cod)]_2$ and Et_2Zn would generate predominantly the corresponding *E*-enolate **6** via 1,4-reduction, which is stabilized through η^6 binding with benzene ring of the substrate. Subsequent transmetalation with zinc species **4** readily reacts with the carbonyl group to form the intramolecular C–C bonds at the α-position, then providing the product *syn*-**2a** with high regioselectivity. On the other hand, the use of higher coordinating solvents such as DMF or DMPU might break the weak η^6 binding of rhodium complex to give *anti*-**2a**, predominantly.

Synthesis of a chiral necic acid lactone of monocrotaline

There are several reports of bioactive natural products that have a 3-hydroxy-2-methyllactone scaffold in the molecular structure. For example, cytospolide K2 [50] containing a 10-membered lactone and feigrisolide [51] containing a 7-membered lactone are known to exhibit cytotoxicity and antimicrobial activity. Moreover, antiviral activity was also confirmed for aggregatin B [52] containing a 7-membered lactone ring, in which the β-position hydroxy group was dehydrated (Figure 1). Monocrotaline is a kind of pyrrolizidine alkaloid and was isolated from seeds of *Crotalaria spectabilis* in 1935 [53]. Monocrotaline is used as compound for pulmonary hypertension model in rats. To date, some groups have reported synthetic methods and its synthetic supply will potentially contribute to hypertension treatment [54-57]. Although there have been a lot of reports of pyrrolizidine scaffolds or necine base, the synthesis of necic acid lactones such as monocrotalic acid is rare (Figure 2). Consequently, we attempted to apply the rhodium-



Scheme 3: Detection of metal-enolate and proposed mechanism of intramolecular cyclization.

catalyzed intramolecular reductive aldol-type reaction to the synthesis of a chiral necic acid lactone that is a part of structural component of monocrotaline.

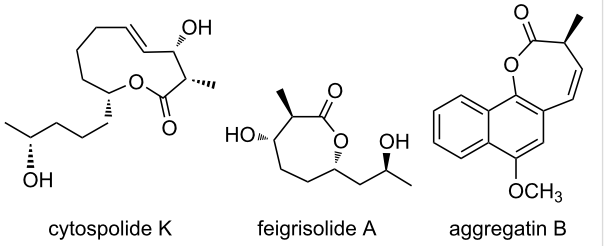


Figure 1: Bioactive natural products bearing a 3-hydroxy-2-methyllactone scaffold.

According to the literature, a Sharpless dihydroxylation of benzyl tiglate (**8**) to form a chiral diol **9** was followed by a Parikh–Doering oxidation to give the corresponding product **10** in 62% yield (Scheme 4) [58,59]. Subsequent acryloylation in the presence of DMAP and hydroquinone gave the intramolecular cyclization starting material (*S*)-**1j** in 61% yield. The transformation of the compound (*S*)-**1j** in the rhodium-catalyzed intramolecular reductive aldol-type cyclization proceeded smoothly and gave the chiral necic acid lactone (2*S*,3*S*,4*R*)-**2j** in 32% yield (Figure 3).

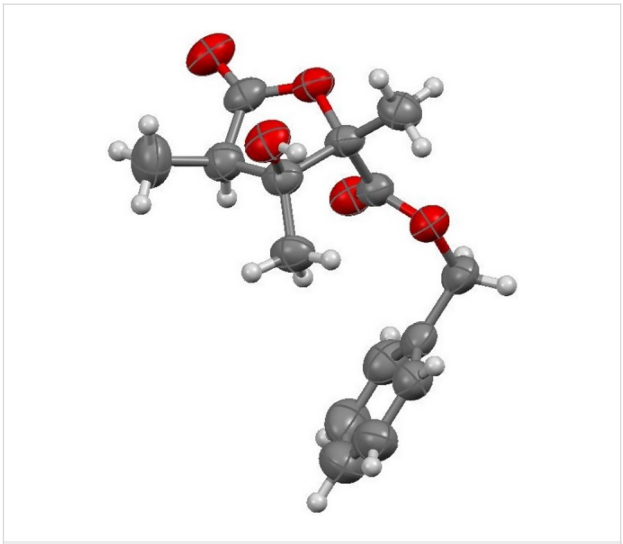


Figure 3: Molecular structure of necic acid lactone (2*S*,3*S*,4*R*)-**2j** in the crystal.

Conclusion

In conclusion, during the development of a rhodium-catalyzed intramolecular reductive cyclization, we found that using $[RhCl(cod)]_2$ improved the diastereomeric ratio of the products compared with other Rh catalysts. It seems that using $[RhCl(cod)]_2$ leads to milder reaction conditions that lead to highly improved diastereomeric ratios. In addition, we demon-

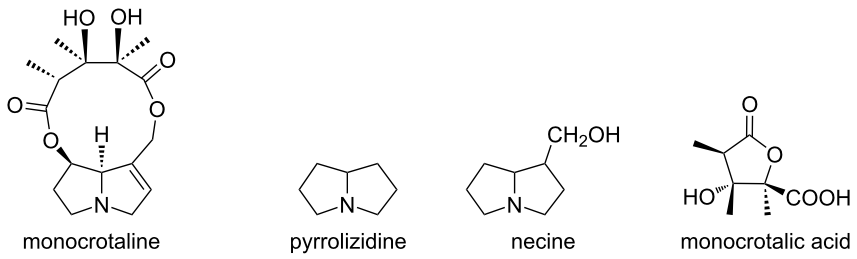
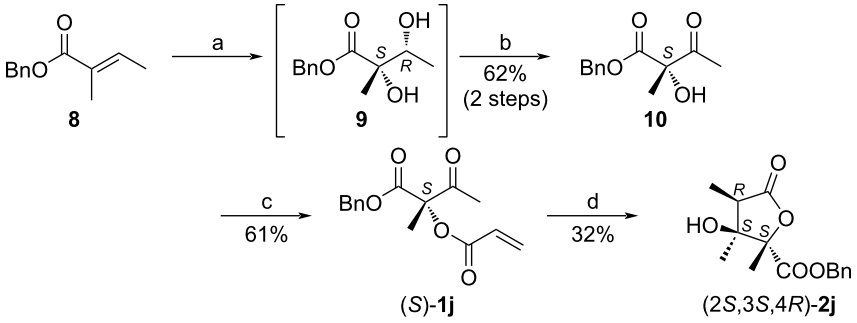


Figure 2: Monocrotaline and its structural components.



Scheme 4: Synthetic route towards chiral necic acid lactone (2*S*,3*S*,4*R*)-**2j**. Conditions: a) $CH_3SO_2NH_2$, AD-mix-β, *t*-BuOH, H_2O. b) SO_3·Py, Et_3N, DMSO, CH_2Cl_2. c) DMAP, CH_2Cl_2, Et_3N, acryloyl chloride, hydroquinone. d) $[RhCl(cod)]_2$, THF, Et_2Zn.

strated a new approach to a necic acid lactone **2j** that is a diastereomer of monocrotalic acid, a key intermediate of monocrotalin.

Supporting Information

Supporting Information File 1

General procedures and analytical data, including copies of ^{1}H NMR, ^{13}C NMR, and X-ray crystallography.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-18-176-S1.pdf]

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Preprint

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