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(Enantio)selective Hydrogen Autotransfer: Ruthenium-Catalyzed Synthesis of Oxazolidin-2-ones from Urea and Diols

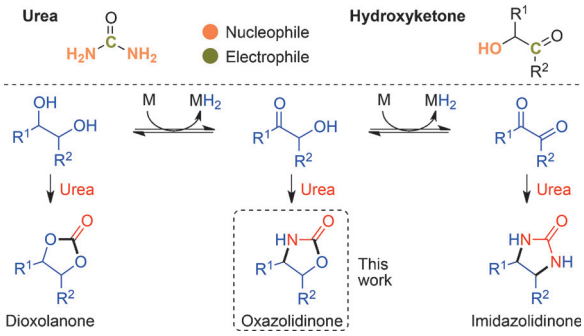
*Miguel Peña-López, Helfried Neumann, and Matthias Beller**

Abstract: *A novel strategy for the synthesis of oxazolidin-2-ones from vicinal diols and urea is described. In this heterocycle synthesis, two different C–O and C–N bonds are sequentially formed in a domino process consisting of nucleophilic substitution and alcohol amination. The use of readily available starting materials and the good atom economy render this process environmentally benign. While this transformation is already highly chemo- and regioselective, we also developed the first asymmetric version of this method using (R)-(+)-MeO-BIPHEP as the chiral ligand.*

A plethora of biologically active compounds contain a heterocyclic system as a central skeleton.[1] Therefore, many methods aimed at the construction of such frameworks have been developed.[2] Traditionally, most of these methods rely on classic nucleophilic substitution reactions and thus result in the formation of significant amounts of waste. Hence, the discovery of more efficient and environmentally friendly processes constitutes an important goal. In this context, metal-catalyzed dehydrogenative coupling reactions offer several benefits. More specifically, the so-called hydrogen autotransfer (or "borrowing hydrogen") approach allows the efficient formation of C–C and C–N bonds from non-activated alcohols.[3] In the last decade, several heterocyclic compounds have also been synthesized by applying such reactions in a sequential manner.[4] Advantageously, water is formed as the only byproduct, and the possibility of using renewable alcohols as the starting materials makes these transformations sustainable.

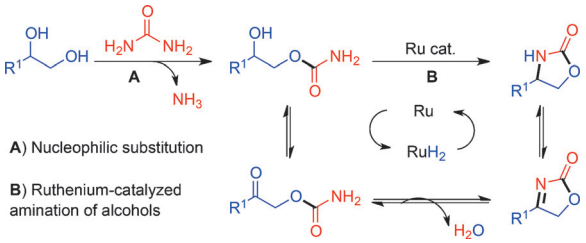
On this basis and following our previous experience, we herein propose the use of ubiquitously available substrates (urea and diols) for the synthesis of valuable heterocycles.[5] Vicinal diols display high versatility in such transformations as they are susceptible to more than one metal-catalyzed dehydrogenation. In general, the starting diol is considered to be a dinucleophile, whereas successive oxidations give rise to electrophilic carbonyl compounds (Scheme 1). Subsequent reactions of such intermediates with urea potentially lead to the formation of different heterocycles, such as dioxolanones, oxazolidinones, and imidazolidinones.

Within these possibilities, the selective synthesis of oxazolidin-2-ones (cyclic urethanes) constitutes a particular challenge because both starting materials behave as nucleophiles and electrophiles. This heterocycle is highly relevant in organic chemistry. For example, it can be used as precursor for the synthesis of naturally occurring amino acids[6] and as a chiral auxiliary in asymmetric synthesis (Evans' oxazolidinones).[7] Furthermore, it is present in several antimicrobials and antibiotics.[8] Although several synthetic strategies have already been published,[9] the further development of new, efficient, and low-cost catalytic procedures remains to be particularly interesting.



Scheme 1. Dehydrogenative metal-catalyzed reaction of urea with vicinal diols.

Based on our knowledge in the area of dehydrogenative processes,[4] we envisioned a novel (chemo)selective synthesis of oxazolidin-2-ones. As shown in Scheme 2, a C–O bond would initially be formed by nucleophilic substitution of urea with one hydroxy group of the diol. Next, a ruthenium-catalyzed dehydrogenation of the second alcohol moiety should provide the corresponding carbonyl compound, which would undergo a condensation with the remaining amino group of the urea moiety, affording the desired C–N bond after reduction with the hydrogen that was initially extracted. It should be noted that this heterocycle synthesis could also take place in reverse order depending on which step is faster



Scheme 2. Ruthenium-catalyzed synthesis of oxazolidin-2-ones from urea and vicinal diols.

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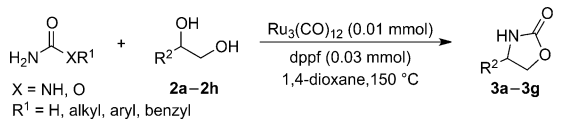
under the applied reaction conditions. Obviously, a high degree of selectivity is required owing to the nucleophilic and electrophilic character of both substrates, which could lead to different heterocyclic compounds and oligomers or polymers. In this context, we herein describe the first highly selective ruthenium-catalyzed synthesis of oxazolidinones from inexpensive urea and vicinal diols by hydrogen autotransfer.

Our investigations began with the optimization of the reaction conditions for the model reaction of urea (**1**, 1 mmol) with 1-phenylethane-1,2-diol (**2a**, 1 mmol), a substrate with two different hydroxy groups (see the Supporting Information, Scheme S1). Based on previous studies by our group,[10] we initially used $[Ru_3(CO)_{12}]$ as the catalyst in combination with different phosphines. Only traces of the desired product were observed under ligand-free conditions, whereas the use of different mono- and bidentate phosphines afforded 4-phenyloxazolidin-2-one (**3a**) selectively in moderate yields (20–52%). Based on these first results, we performed a more detailed optimization of the best ligand system (dppf = 1,1′-bis(diphenylphosphino)ferrocene). As shown in the Supporting Information, Table S1, we studied different ruthenium precursors, catalyst loadings, ratios of **1**/**2a**, and additives and varied other critical parameters, such as the solvent, temperature, and reaction time. Finally, we found that the reaction of urea (**1**, 1 mmol) and **2a** (0.5 mmol) was most efficient in the presence of $[Ru_3(CO)_{12}]$ (0.01 mmol) and dppf (0.03 mmol) in 1,4-dioxane at 150°C for 22 h, which enabled the isolation of **3a** in 76% yield (Table 1, entry 1). Considering that at least four steps are involved in this reaction sequence, the optimized yield indicates that each individual transformation proceeds with high efficiency, while the formation of water and ammonia as the only byproducts renders this process atom-efficient and environmentally benign. Gratifyingly, the reaction proceeded with chemoselectivity as **3a** was almost exclusively obtained with only traces of the cyclic carbonate (8% yield, see Scheme 1). Furthermore, the 4-substituted product was formed as the only regioisomer, which suggests that nucleophilic substitution preferably occurs with the terminal alcohol and intramolecular amination with the internal one.

To expand the scope of this method, we next evaluated the reactivity of different terminal diols. Electron-deficient styrene diol derivatives, such as compounds **2b** and **2c**, were effectively converted into the corresponding oxazolidin-2-ones **3b** and **3c** (71 and 65% yield, respectively; Table 1, entries 2 and 3). Analogously, this reaction can also be extended to aryl diols with electron-donating groups such as **2d**, which afforded **3d** in 73% yield (entry 4). On the other hand, the reaction of benzyl derivative **2e** also took place regioselectively to give 4-benzyloxazolidin-2-one (**3e**) in a good yield of 64% (entry 5). Aside from aromatic substrates, this reaction also worked well with aliphatic terminal diols. Thus, the reactions of hexane- and octane-1,2-diol (**2f** and **2g**) under the initially established conditions led to the desired products in similar yields (69 and 66%; entries 6 and 7). Finally, we were interested in studying the behavior of unsaturated oct-7-ene-1,2-diol (**2h**). In this case, reduction of the terminal C=C bond was also observed, providing the saturated oxazolidin-2-one **3g** in 65% yield (entry 8). The well-known ability of ruthenium complexes to promote the isomerization or reduction of multiple bonds[11] implies that the hydrogen extracted in the first step is used in both imine and C=C bond reduction.

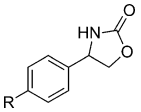
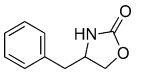
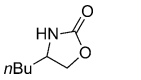
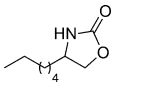
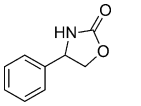
At this point, our catalytic system was applied to the reaction of 1-phenylethane-1,2-diol (**2a**) with different substituted ureas and carbamates (Table 1). Here, our initial objective was the synthesis of N-protected oxazolidin-2-ones by using N-monosubstituted ureas as the starting materials. Unfortunately, the ruthenium-catalyzed reaction of **4a**–**4d** using the conditions previously developed provided the free (NH) oxazolidin-2-one **3a** in moderate yields (45–56%; entries 9–12). These results suggest that the primary amine is a better leaving group than ammonia in the initial nucleophilic substitution step, and that the amination of the secondary alcohol takes place preferably with the free NH_2 group. The presence of the primary amine in the reaction

Table 1: Ruthenium-catalyzed synthesis of 4-substituted oxazolidin-2-ones (**3a**–**3g**) from ureas or carbamates (**1**, **4**, **5**) and terminal diols (**2a**–**2h**).[a]



X = NH, O; R^1 = H, alkyl, aryl, benzyl

2a–**2h** **3a**–**3g**

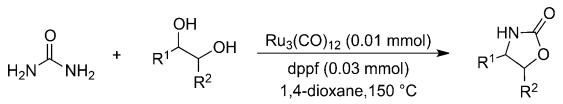
Entry	XR^1	R^2	Product		Yield [%][b]
1	NH_2 (**1**)	phenyl (**2a**)		(**3a**)	76
2	NH_2 (**1**)	*p*-ClC_6H_5 (**2b**)		(**3b**)	71
3	NH_2 (**1**)	*p*-$F_3CC_6H_5$ (**2c**)		(**3c**)	65
4	NH_2 (**1**)	*p*-$MeOC_6H_5$ (**2d**)		(**3d**)	73
5	NH_2 (**1**)	benzyl (**2e**)		(**3e**)	64
6	NH_2 (**1**)	*n*-butyl (**2f**)		(**3f**)	69
7	NH_2 (**1**)	*n*-hexyl (**2g**)		(**3g**)	66
8	NH_2 (**1**)	5-hexenyl (**2h**)		(**3g**)	65[c]
9[d]	NHMe (**4a**)	phenyl (**2a**)		(**3a**)	56
10[d]	NHEt (**4b**)	phenyl (**2a**)		(**3a**)	54
11[d]	NHPh (**4c**)	phenyl (**2a**)		(**3a**)	49
12[d]	NHBn (**4d**)	phenyl (**2a**)		(**3a**)	45
13[d]	OMe (**5a**)	phenyl (**2a**)		(**3a**)	62
14[d]	O*t*Bu (**5b**)	phenyl (**2a**)		(**3a**)	71
15[d]	OPh (**5c**)	phenyl (**2a**)		(**3a**)	69
16[d]	OBn (**5d**)	phenyl (**2a**)		(**3a**)	72

[a] Unless otherwise specified, all reactions were carried out with **1** (1.0 mmol), **2** (0.5 mmol), $Ru_3(CO)_{12}$ (0.01 mmol), and dppf (0.03 mmol) in 1,4-dioxane (1 mL) at 150°C for 22 h. [b] Yields of isolated products. [c] The maximum amount of product would be 0.25 mmol. In addition, the formation of unsaturated isomers in 10% yield was observed. [d] Urea or carbamate (**4** or **5**, 1.5 mmol).

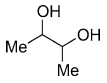
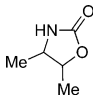
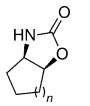
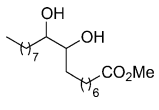
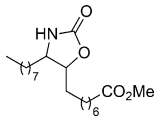
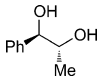
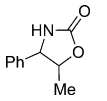
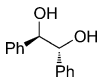
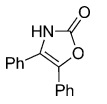
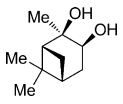
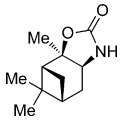
medium also promotes further side reactions; therefore, higher amounts of urea were required to achieve acceptable yields. Next, we performed the reaction with carbamates as urea analogues. The reaction of **2a** with **5a**–**5d** provided the heterocycle **3a** in good yields (62–72%; entries 13–16). Here, the alcohol resulting from substitution does not participate in undesired reactions that decrease the yield.

To demonstrate the broad applicability of this synthetic strategy, our method was tested with internal diols. Unlike in the previous study, here the similar reactivity of both hydroxy groups could lead to a lack of selectivity, resulting in a mixture of compounds as shown in Scheme 1. On this basis, we initially performed the reaction of urea (**1**, 1 mmol) with butane-2,3-diol (**6a**, 0.5 mmol) in the presence of $[Ru_3(CO)_{12}]$ (0.01 mmol) and dppf (0.03 mmol) in 1,4-dioxane at 150°C. Satisfactorily, the desired product, 4,5-dimethyloxazolidin-2-one (**7a**), was isolated in 65% yield as a mixture of diastereoisomers (60:40 d.r.), while the corresponding 1,3-dioxolan-2-one and imidazolidin-2-one were formed in only 4 and 10% yield, respectively (Table 2, entry 1). We then decided to study the reactivity of cyclic diols such as **6b** and **6c**. In both cases, the oxazolidin-2-ones **7b** and **7c** were formed as the major products and with good diastereoselectivity (48 and 56%; entries 2 and 3), although the amount of the mentioned side products increased. Alternatively, experiments with the long-chain substrate **6d** and (1*R*,2*R*)-1-phenylpropane-1,2-diol (**6e**) gave rise to the 4,5-disubstituted heterocycles **7d** and **7e** as complex mixtures of regio- and diastereoisomers in moderate yields (45 and 42%, respectively; entries 4 and 5). Here, cyclic carbonates were observed only as side products. However, the reaction of urea (**1**) with (*R*,*R*)-hydrobenzoin (**6f**) provided the unsaturated oxazolidinone **7f** in 43% yield (entry 6). The double bond formed after the condensation reaction isomerizes to a conjugated olefin, which is not reduced under these conditions. Lastly, we studied the reactivity of an internal diol with a tertiary alcohol in its structure, thereby avoiding the formation of imidazolidin-2-ones owing to the inability of that moiety to undergo dehydrogenative reactions. The reaction of terpene diol **6g** resulted in the formation of cyclic urethane **7g** and the corresponding carbonate in moderate yields (45 and 41%, respectively; entry 7). The structure of the only diastereoisomer formed in this novel cyclization process was confirmed by X-ray crystallography (see the Supporting Information).

Table 2: Ruthenium-catalyzed synthesis of 4,5-disubstituted oxazolidin-2-ones (**7a**–**7g**) from urea (**1**) and internal diols (**6a**–**6g**).[a]



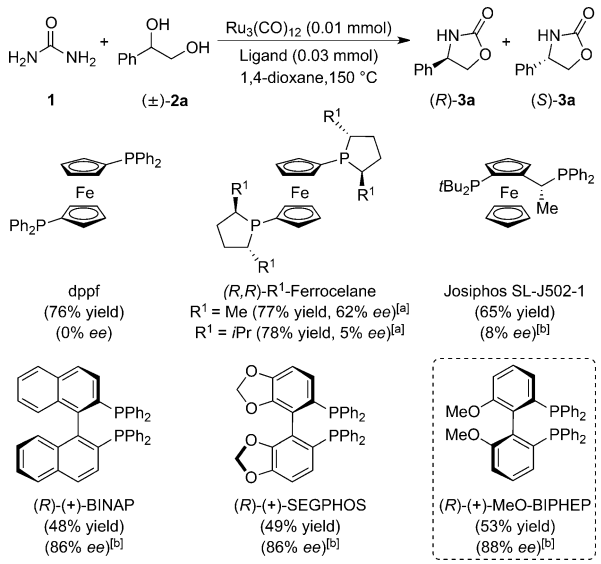
1 **6a**–**6g** **7a**–**7g**

Entry	Diol		Product		Yield [%][b]
1		(**6a**)		(**7a**)	65 (4/10)[c,d]
2		(**6b**, $n=1$)		(**7b**)	48 (15/19)[c]
3		(**6c**, $n=2$)		(**7c**)	56 (3/21)[c]
4		(**6d**)		(**7d**)	45 (23)[e,f]
5		(**6e**)		(**7e**)	42 (21)[e,f]
6		(**6f**)		(**7f**)	43 (32)[e]
7		(**6g**)		(**7g**)	45 (41)[e]

[a] Unless otherwise specified, all reactions were carried out with **1** (1.0 mmol), **6** (0.5 mmol), $Ru_3(CO)_{12}$ (0.01 mmol), and dppf (0.03 mmol) in 1,4-dioxane (1 mL) at 150°C for 22 h. [b] Yields of isolated products. [c] The isolated yield of the corresponding 1,3-dioxolan-2-one/imidazolidin-2-one is given in parentheses. [d] **7a**: 60:40 d.r. [e] The yield of isolated cyclic carbonate is given in parentheses. [f] The oxazolidinones were isolated as complex mixtures of regio- and diastereoisomers.

Finally, in an effort to render this procedure more synthetically relevant, we considered the development of the corresponding asymmetric version. One of the most important applications of oxazolidin-2-ones in organic chemistry is their use as chiral auxiliaries.[7] For this purpose, these compounds need to be available in enantiopure form, and despite the synthetic strategies published thus far,[12] the discovery of straightforward, selective, sustainable, and more efficient methods is still of high importance. Based on the postulated mechanism (Scheme 2), the key step for the generation of the stereogenic carbon center would be the reduction of the intermediate imine with the hydrogen that is initially extracted. Chiral variants of hydrogen autotransfer processes have rarely been reported,[13] which is probably due to the high temperatures that are required for such reactions, but usually lead to a decrease of the enantiomeric excess.

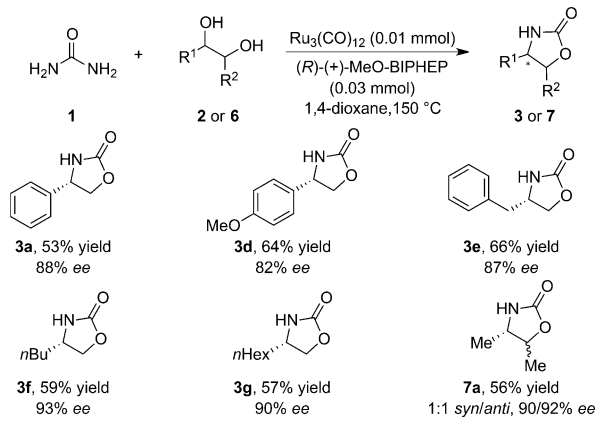
To develop such an asymmetric variant, we considered the reaction of urea (**1**) with racemic 1-phenylethane-1,2-diol (**2a**) as a model transformation as an asymmetric center is formed at the C4 position. As shown in Scheme 3, different chiral ligands were studied in combination with $[Ru_3(CO)_{12}]$. Obviously, the previously used dppf ligand provided 4-phenyloxazolidin-2-one (**3a**) as a racemic mixture. In line with this example, chiral ferrocenyl phosphines were tested and found to lead to similar yields but moderate enantioselectivities (5–62% *ee*). Encouraged by these results, we analyzed the effects of ligands with axial chirality. Among



Scheme 3. Ligand screen for the enantioselective ruthenium-catalyzed synthesis of 4-phenyloxazolidin-3-one (**3a**). Yields of isolated products are given. [a] (*R*)-**3a** was formed as the major enantiomer. [b] (*S*)-**3a** was formed as the major enantiomer.

various readily available diphosphines, such as (*R*)-(+)-BINAP and (*R*)-(+)-SEGPHOS, (*R*)-(+)-MeO-BIPHEP enabled the formation of (*S*)-**3a** at 150 °C in 53% yield and excellent 88% *ee* (94:6 enantiomeric ratio, Scheme 3).

With a suitable chiral catalytic system in hand, we studied the enantioselective reaction of urea (**1**) with other diols. Gratifyingly, the oxazolidin-2-one **3d** was obtained in a good yield of 64% and 82% *ee*, whereas the benzyl derivative gave similar results (**3e**, 66% yield, 87% *ee*; Scheme 4). Furthermore, this asymmetric reaction can also be applied to terminal alkyl-substituted diols as shown by the formation of products **3f** and **3g** (59 and 57% yield, 93 and 90% *ee*). Finally, an internal diol was also tested. The amination reaction afforded the disubstituted heterocycle **7a** in 56% yield. Whereas the two diastereoisomers were formed in equal amounts (1:1 *syn*/*anti*), the enantioselectivity of the reaction was excellent (90 and 92% *ee*, Scheme 4). These results suggest that highly stable catalytic species are involved in this reaction that enables the enantioselective formation of stereogenic carbon centers even at such high temperatures.



Scheme 4. Enantioselective ruthenium-catalyzed synthesis of oxazolidin-2-ones (**3**–**7**). Yields of isolated products are given.

In conclusion, we have described a novel domino process for the ruthenium-catalyzed synthesis of oxazolidin-2-ones from urea and vicinal diols. This atom-efficient method allows the sequential formation of C–O and C–N bonds in good yields using a commercially available catalytic system ($Ru_3(CO)_{12}$/dppf). The use of simple substrates and the formation of water and ammonia as the only byproducts render this straightforward process environmentally benign. While these transformations generally proceed with high chemo- and regioselectivity, the use of an appropriate chiral ligand enabled the development of an asymmetric version.

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Keywords: diols · domino reactions · enantioselectivity · oxazolidinones · ruthenium catalysis

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