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Synthesis of 2-oxazolidinones by salen-Co-complexes catalyzed oxidative carbonylation of β-amino alcohols

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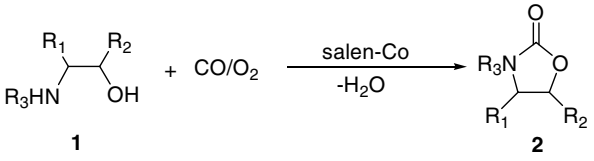
Abstract—2-Oxazolidinones are synthesized in high yield by oxidative carbonylation of β-amino alcohols using salen-Co(II)/NaI or salen-Co(III)-I as a catalyst and using CO as the carbonyl source. Studies of functional group compatibility using a series of substituted salen-Co(II) or salen-Co(III)-I complexes demonstrate a broad tolerance of functionality during the carbonylation reaction.

2-Oxazolidinones and their derivatives have attracted much attention due to the appearance of this functionality as intermediates in fine chemicals, pharmaceuticals, pesticides and herbicides.[1] Particularly, the heterocyclic derivatives of β-amino alcohols have been widely used as chiral auxiliaries in asymmetric syntheses.[2–5] Currently, these compounds are mainly manufactured by the phosgenation of β-amino alcohols. However, the use of phosgene in the synthesis of 2-oxazolidinones precludes its widespread application in laboratory and industrial settings due to its serious environmental issues.[6] Therefore, the use of an alternative to phosgene in the synthesis of 2-oxazolidinones is highly desirable to eliminate the application of phosgene altogether. Several methods for phosgene-free routes have been developed, including the substitute of diethyl carbonate and oxidative carbonylation.[7–10] However, the use of carbonates as a phosgene substitute is relatively expensive for commercial application, and the carbonates are generally prepared by making use of phosgene or its substitutes.[11] The oxidative carbonylation is particularly attractive from the standpoint of atom economy and environmental concerns, since it employs β-amino alcohols, carbon monoxide and oxygen as starting materials and produces the desired compounds and harmless H_2O as side product. Until now, only few reports have been described using this catalytic process.[7–9] However, thus far the reported research mostly focuses on the precious metal Pd, where the expensive palladium catalysts are difficult to be separated and reused. As a result, it is necessary to develop a new catalytic system to produce the important N-containing carbonyl compounds.

In this Letter, we wish to report a highly efficient catalytic system without precious metal Pd for the oxidative carbonylation of β-amino alcohols to 2-oxazolidinones, in the presence of salen-Co(II)/NaI or salen-Co(III) complexes (Scheme 1). To the best of our knowledge, this is the first catalytic process to synthesize 2-oxazolidinones with salen-Co(II)/NaI or salen-Co(III) complexes as catalysts. Since the salen-Co(II) complexes and salen-Co(III) complexes are prepared easily from the commercially available salen ligands, this methodology represents a convenient means of obtaining 2-oxazolindinones.



1 2

Scheme 1. Synthesis of 2-oxazolidinones by oxidative carbonylation.

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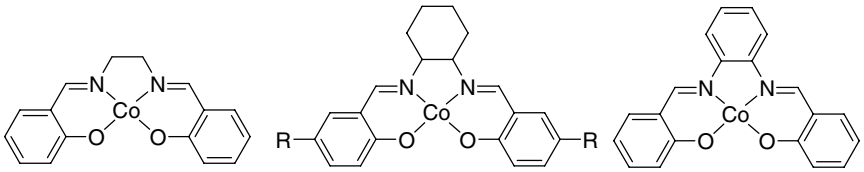
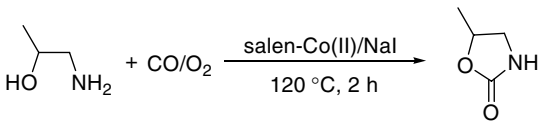


3 **4: R=H; 5: R=Br; 6: R=NO_2** **7**

In our initial investigation, *i*-propanol amine was used as the substrate to form 5-methyloxazolin-2-one with salen-Co(II) complexes **3**–**7** acting as the catalysts.[12] The first set of results reinforced the notion that the desired compound was always obtained as a predominant product (Table 1, entries 1–5). It was noteworthy that the high efficiency of the salen-Co(II)/NaI promoter catalytic system was applicable to the oxidative carbonylation of isopropanolamine under the optimal reaction conditions (the molar ratio of substrates/catalyst = 200, temperature 120 °C, time 2 h).

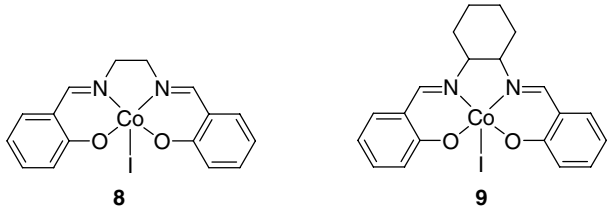
We then tested the oxidative carbonylation of a series of β-amino alcohols over the above mentioned salen-Co(II)/NaI catalytic system. It was found that this methodology is perfectly applicable to primary amino alcohols, affording the corresponding 2-oxazolidinones in high yield. The results are summarized in Table 2. As can be seen, ethanol amine, *i*-propanol amine and 2-amino-butanol showed excellent conversion and yield; however, other β-amino alcohols were slightly less reactive than that primary aliphatic amino alcohol. When 2-aminophenol (**1i**) was used as the reaction substrate, only traces of product were observed. We derived the main product 2-aminophenoxazin-3-one (92% isolated yield) from an oxidative dimerization process without CO incorporation.[9b]

Table 1. The catalytic performances of salen-Co(II) complexes **3**–**7** towards oxidative carbonylation of *i*-propanol amine with or without NaI as a promoter[a]



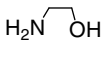
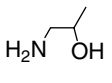
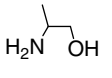
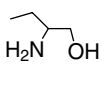
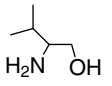
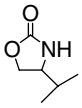
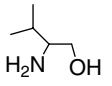
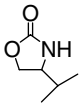
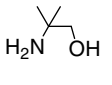
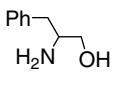
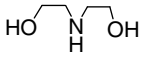
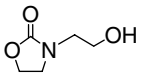
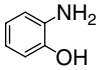
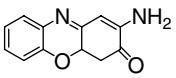
Entry	Catalyst	Conv. (%)	Yield[c] (%)
1	**3**[b]	100	72[d]
2	**4**[b]	100	82[d]
3	NaI	—	—
4	**3**	100	94
5	**4**	99	91
6	**5**	99	86
7	**6**	100	95
8	**7**	100	94

[a] Reaction condition: 0.05 mmol of salen-Co(II), 0.2 mmol of NaI, 10 mmol of β-amino alcohols, 1,4-dioxane (6 ml), $P_{CO} = 5.7$ MPa, $P_{O_2} = 0.3$ MPa, 120 °C for 2 h.
[b] Without NaI.
[c] Isolated yield.
[d] GC yield.

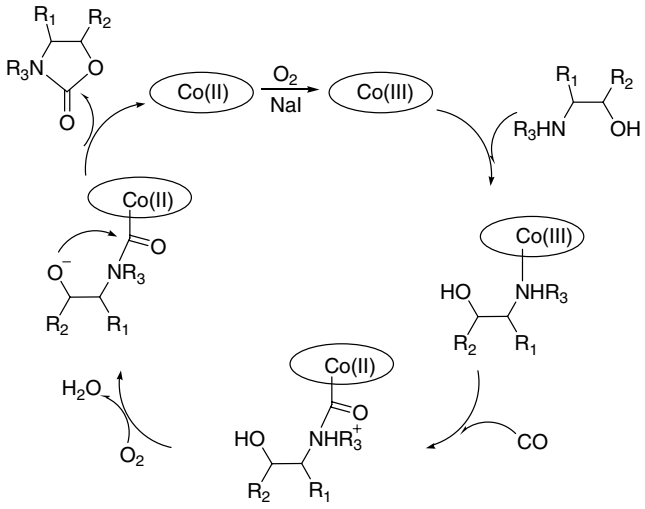


8 **9**

Table 2. Synthesis of 2-oxazolidinones catalyzed by salen-Co(II)/NaI catalyst system[a]

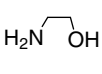
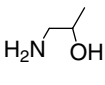
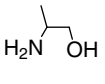
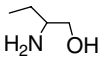
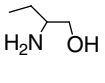
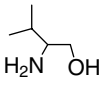
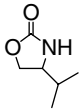
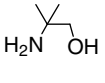
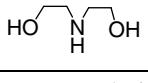
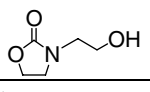
Entry	**1**	Substrate	Product	Yield[e] (%)
1	**1a**			89
2	**1b**[b]			94
3	**1c**			96
4	**1d**			94
5	**1e**[c]			76
6	**1e**[c,d]			91
7	**1f**			87
8	**1g**[c]			84
9	**1h**[d]			74
10	**1i**			92

[a] Reaction condition: 0.05 mmol of salen-Co(II) complex **3**, 0.2 mmol of NaI, 10 mmol of β-amino alcohols, 1,4-dioxane (6 ml), $P_{CO} = 5.7$ MPa, $P_{O2} = 0.3$ MPa, 120 °C for 2 h.
[b] Racemic substrate.
[c] *S* enantiomer.
[d] Salen-Co(II) complex **4** was used.
[e] Isolated yield.



Scheme 2. The proposed mechanism of oxidative carbonylation reaction catalyzed by salen-Co complexes.

Table 3. Synthesis of 2-oxazolidinones catalyzed by salen-Co(III) complexes directly[a]

Entry	1	Substrate	Product	Yield[f] (%)
1	**1a**[b,c]			86
2	**1b**[b,c]			93
3	**1c**			94
4	**1d**[c,d]			73
5	**1d**[d]			90
6	**1e**[e]			91
7	**1f**			87
8	**1h**			72

[a] Reaction condition: 0.05 mmol of salen-Co(III) complex **9**, 10 mmol of β-amino alcohols, 1,4-dioxane (6 ml), $P_{CO} = 5.7$ MPa, $P_{O_2} = 0.3$ MPa, 120 °C for 3 h.
[b] Salen-Co(III) complex **8** was used.
[c] Reaction time, 2 h.
[d] Racemic substrate.
[e] *S* enantiomer.
[f] Isolated yield.

Until now, the mechanism of oxidative carbonylation of amine is not well understood. Based on the previous reports,[8d,13] a possible overall mechanism of this new and transition-metal Co catalytic oxidative carbonylation process is proposed in Scheme 2. In the presence of NaI and dioxygen, active salen-Co(III)-I species are generated and then reacted with the NH_2 of the β-amino alcohols and CO to produce carbonyl-type complexes,[13] which further react with the OH of the β-amino alcohols to produce 2-oxazolidinones. Consequently, in an attempt to gain insight into the mechanism, we tested the catalytic activity of salen-Co(III) complexes[14] for the oxidative carbonylation of β-amino alcohols. We observed that oxidative carbonylation proceeded uneventfully without any promoter, such as NaI. (The results are summarized in Table 3.) These results strongly suggest that the salen-Co(III) complex is the active catalyst species. Interestingly, the diethanolamine (Table 2, entry 9 and Table 3, entry 8) was firstly converted to the corresponding 2-oxazolidinones through oxidative carbonylation reaction.

In conclusion, we have developed an efficient oxidative carbonylation reaction catalyzed by salen-Co(II)/NaI catalytic system or salen-Co(III) complexes. This atom-economical methodology represents a valuable and environmentally benign non-phosgene alternative to the use of toxic phosgene or expensive diethyl carbonate. The application of salen-Co complexes to other carbonylation reactions, and further understanding of the reaction mechanism are currently being investigated in our laboratory.

Acknowledgements

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12. All oxidative carbonylation experiments were carried out in a 100 ml autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, β-amino alcohols (10 mmol), catalyst, salen-Co (0.05 mmol), NaI (0.20 mmol) and solvent (1,4-dioxane, 6 ml) were charged into the reactor. Then the autoclave was pressurized with carbon monoxide and oxygen to a total pressure of 6.0 MPa (CO purity 99.9% 5.7–5.8 MPa and O_2 99.99% 0.2–0.3 MPa). The autoclave was placed in an oil bath pre-heated at 120 °C, and the whole reaction mixture was stirred for 2 h. After the reaction, the autoclave was cooled, and excess gas was purged slowly. The products were easily purified by column chromatography on silica gel.
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