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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 12419–12423

A novel way to chiral 2-oxazolidinones: selenium-catalyzed cyclocarbonylation of 2-aminoethanols

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Received 8 May 2007; revised 16 September 2007; accepted 18 September 2007
Available online 22 September 2007

Abstract—Selenium-catalyzed cyclocarbonylation of 2-aminoethanols with CO under atmospheric pressure at 30 °C afforded 2-oxazolidinones in excellent yields without any other co-catalyst. The method was then applied to the syntheses of chiral 2-oxazolidinones and no racemization was detected.

1. Introduction

2-Oxazolidinones are a very important class of heterocyclic compounds. Some molecules containing the 2-oxazolidinone moiety have shown antibacterial activity,[1] and the chiral 2-oxazolidinones have been used as chiral auxiliaries in a wide range of asymmetric reactions.[2–10] A variety of conventional syntheses of 2-oxazolidinones have been developed from 2-aminoethanols as starting materials. Syntheses of 2-oxazolidinones were carried out by cyclization of alkyl or aryl carbamates under either acidic[11] or basic[12,13] conditions, cyclization of triphenylphosphonium salts[14] or *N*-nitroso compounds,[15] and carbonylation of 2-aminoethanols with phosgene,[16,17] diphosgene,[18,19] triphosgene,[20,21] urea,[22] or cyanates.[17,23] Most of these preparative methods need drastic conditions (high temperature or strong acid or base) or toxic compounds such as phosgene or phosgene derivatives.

Nowadays, as an alternative, direct carbonylation of 2-aminoethanols with carbon monoxide is an attractive and effective way to prepare these heterocyclic compounds in view of environmental concerns. Recently, many efforts have been addressed to the transition metal catalyzed intramolecular cyclocarbonylation of 2-aminoethanols.[24–30] Although some advancement has been achieved, the reaction conditions are still stern and the catalysts used are usually expensive. The cyclocarbonylation reactions in the presence of elemental sulfur have also been investigated, but equivalent moles of sulfur and base or otherwise relatively stern reaction conditions are required.[31,32] Furthermore, to our best knowledge, catalytic carbonylation reactions of chiral 2-aminoethanols with carbon monoxide to obtain chiral 2-oxazolidinones have not been investigated.

Selenium-catalyzed carbonylation reaction of 2-aminoethanols has been proved to be an excellent method for the cheap and easily available catalyst, mild reaction conditions, and reaction process phase transfer property.[33] This method was first reported by Koch and Perrotti in 1974,[34] and then improved by Sonoda, in whose works the reaction proceeded under atmospheric pressure at room temperature but suffered from large amounts of strong base.[35] In the course of our ongoing studies on the selenium-catalyzed carbonylation reactions using CO, we had investigated the influence of the oxidants to the cyclocarbonylation reaction of ethanolamine under pressurized conditions at 150–160 °C and found that molecular oxygen served as the best oxidants.[36] Most recently, we are surprised to find that 2-oxazolidinones can be obtained in excellent yields in the absence of any basic compound under mild conditions (1 atm, 30 °C). No racemization has been detected when we apply this method to the syntheses of chiral 2-oxazolidinones. Herein we report a first synthesis of both racemic and chiral 2-oxazolidinones using the selenium-catalyzed carbonylation of corresponding 2-aminoethanols with bubbling CO in CH_3CN under atmospheric pressure at 30 °C for the first time.

2. Results and discussion

2.1. Carbonylation of ethanolamine under various conditions

Ethanolamine (**1a**) was treated with bubbling mixed gas of carbon monoxide and oxygen in the presence of 5 mol %

Keywords: Chiral 2-oxazolidinones; 2-Aminoethanols; Carbon monoxide; Selenium.
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0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.037

of selenium in acetonitrile at 30 °C for 8 h. Oxidative carbonylation of **1a** proceeded efficiently to give 2-oxazolidinone (**2a**) in 93% yield (Table 2, entry 1). Reaction conditions of **1a** were examined at atmospheric pressure (Table 1). When protic solvents such as CH_3CH_2OH and H_2O were used as solvents at 30 °C, the selenium did not dissolve during the bubbling of CO through the media and so, no carbonylation of **1a** occurred (Table 1, entries 1 and 2). The reaction proceeded to some extent in aprotic solvents such as tetrahydrofuran (THF), acetone, and ethylene glycol diethyl ether (EGDE) (Table 1, entries 3–5). When CH_3CN and *N*,*N*-dimethylformamide (DMF) were used as the carbonylation solvents, the reaction went smoothly and gave excellent yields of 2-oxazolidinone (Table 1, entries 6 and 7). It is noteworthy that elemental selenium dissolved much more slowly in ethylene glycol diethyl ether than in THF or in acetone, but the subsequent oxidation carbonylation process was faster. An increase of the concentration of the substrate by three times in the reaction system decreased the yield of 2-oxazolidinone, but not severely (Table 1, entry 8). Elevated temperature at 50 °C was favorable to the carbonylation process on account of the shortened reaction time (Table 1, entry 9). However, a further elevation of the temperature to 70 °C decreased the yield of **2a** (Table 1, entry 10). Oxygen was an excellent oxidant to the current carbonylation. Although both hydrogen peroxide and DMSO (CH_3SOCH_3) were effective oxidants in our previous trials,[36] they showed poor, or even in the worst, and no activity under current reaction conditions (Table 1, entries 11 and 12, respectively). Despite the fact that the cyclocarbonylation reaction went smoothly without any other additional bases as co-catalyst, it was proved that tertiary amines such as triethylamine could promote the present reaction to some extent. For example, carbonylation process in DMF gave only 52% yield of 2-oxazolidinone at 18 °C in 8 h while 84% yield of 2-oxazolidinone was produced in the presence of 1 equiv of triethylamine (Table 1, entries 13 and 14, respectively). Moreover, the carbonylation reaction at 30 °C finished in 5 h in the presence of 1 equiv triethylamine (3 h faster than that without triethylamine) and gave 95% yield of 2-oxazolidinone (Table 1, entry 15). On the one hand, triethylamine promoted the present carbonylation reactions. On the other hand, it brought other problems to the process besides economic considerations. Due to the stabilization effect of triethylamine to the selenium-containing intermediates and active species generated in the reaction system, it became more difficult to precipitate selenium thoroughly by oxygen oxidation, and usually, the selenium-containing intermediates left in the mother liquid consequently brought an bothersome color to the products. The selenium catalyst remained its activity when it was recycled (Table 1, entries 16 and 17 for the first recycling and the second recycling of the catalyst, respectively).

Table 1. Carbonylation of ethanolamine (**1a**) to 2-oxazolidinone (**2a**)

Entry[a]	Solvent	Oxidant	Temp (°C)	Time (h)	Yield (%)
1	EtOH	O_2	30	8	0
2	H_2O	O_2	30	8	0
3	THF	O_2	30	8	63
4	Acetone	O_2	30	8	57
5	EGDE[b]	O_2	30	8	78
6	DMF[c]	O_2	30	8	93
7	CH_3CN	O_2	30	8	93
8[d]	DMF	O_2	30	15	86
9	CH_3CN	O_2	50	6	94
10	CH_3CN	O_2	70	8	56
11	CH_3CN	H_2O_2	30	10	11
12	CH_3CN	DMSO	30	8	0
13	DMF	O_2	18	8	52
14[e]	DMF	O_2	18	8	84
15[e]	CH_3CN	O_2	30	5	95
16[f]	CH_3CN	O_2	30	8	92
17[g]	CH_3CN	O_2	30	8	93

[a] Reaction conditions: ethanolamine, 10 mmol; Se, 0.5 mmol; solvent, 10 ml; bubbling CO and O_2 (v/v=8:1), 1 atm.
[b] EGDE=ethylene glycol diethyl ether.
[c] DMF=*N*,*N*-dimethylformamide.
[d] Ethanolamine of 40 mmol was delivered.
[e] Triethylamine of 10 mmol was added.
[f] Recycled catalyst for the first time.
[g] Recycled catalyst for the second time.

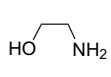
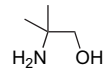
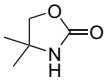
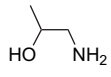
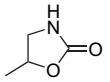
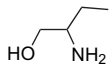
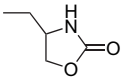
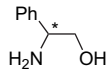
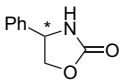
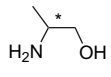
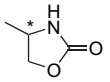
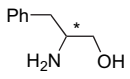
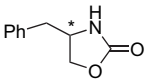
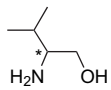
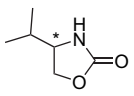
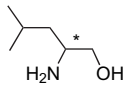
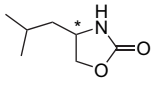
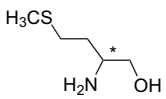
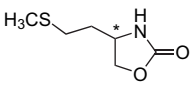
2.2. Carbonylation of substituted 2-aminoethanols

Various substituted 2-aminoethanols including chiral 2-aminoethanols were treated in the similar way as ethanolamine and some representative results are listed in Table 2. 2-Oxazolidinones were consistently obtained in excellent yields (90–96%) within 8–9 h. Despite of the generality of the present catalytic system, reaction times revealed that 2,2-dimethyl ethanolamine and phenylglycinol were a little less reactive (Table 2, entries 2 and 5, respectively) than other substrates employed. This phenomenon may be attributed to the steric effect of the relatively large substituents contained in these two molecules. For **2e**, **2g**, and **2j**, the enantiomeric excess was analyzed by HPLC[37] and as expected, no racemization of the products was detected (>99% ee). This made our present method a powerful tool to obtain useful chiral auxiliaries of this kind. Presently, their synthesis needs two steps: the acylation of amino group and the intramolecular cyclization.[38] Usually, the reaction conditions are stern and the atom economy is low. Among the compounds synthesized, **2g** and **2h** are well known as Evans Reagents and widely used in asymmetric synthesis. No reaction occurred when the present methodology was applied to the carbonylation reaction of 2-aminophenol.

2.3. Proposed pathway of the carbonylation reaction

A reaction process involving a phase transfer phenomenon of the catalyst[33] was presented during the above-discussed reactions. Prior to the introduction of CO into the reaction mixture, the catalytic system was heterogeneous and the catalyst selenium was observed as a powder. As the reaction proceeded the selenium was completely dissolved and the system became homogeneous. When the reaction was quenched by stopping the bubbling of CO but continuing the introduction of O_2, the light-yellowish selenium species was oxidized to form a gray selenium precipitate which can be easily recovered. These results suggested that the present catalytic system was bestowed with advantages of both homogeneous and heterogeneous catalysis. The reason for the dissolvation of elemental selenium during the reaction process could be the in situ formation of SeCO, a key intermediate in selenium-catalyzed carbonylation and/or reduction reactions.[39,40] Ethanolamine could attack SeCO to form the ammonium intermediate **I** (Scheme 1), which could subsequently undergo intramolecular nucleophilic replacement to give 2-oxazolidinone and salt of hydrogen selenide

Table 2. Carbonylation of aminoethanols to 2-oxazolidinones

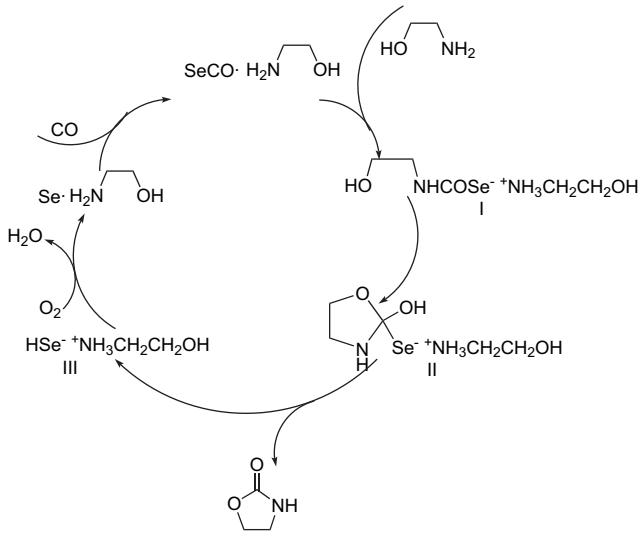
Entry[a]	Config	Reactant	Cyclic product	Isolated yield (%)	Product's mp (°C) (references)
1	—	 (**1a**)	 (**2a**)	93	91–92 (88–89[26])
2[b]	—	 (**1b**)	 (**2b**)	93	53–55 (55.6–56.4[42])
3	DL	 (**1c**)	 (**2c**)	96	Oil
4	DL	 (**1d**)	 (**2d**)	96	Oil
5[b]	D	 (**1e**)	 (**2e**)	90	132–133 (132–133[43])
6	D	 (**1f**)	 (**2f**)	93	58–60 (oil[26])
7	L	 (**1g**)	 (**2g**)	93	87–88 (87–88[26])
8	L	 (**1h**)	 (**2h**)	95	73 (69–70[26])
9	L	 (**1i**)	 (**2i**)	96	Oil
10	L	 (**1j**)	 (**2j**)	96	Oil

[a] Reaction conditions: aminoethanols, 10 mmol; Se, 0.5 mmol; CH_3CN, 10 ml; bubbling CO and O_2 (v/v=10:1), 1 atm; 30 °C; 8 h.
[b] Reaction for 9 h.

III. Further oxidation of **III** could recover the elemental selenium and release a molecule of water. We do not believe that triethylamine is essential to the present reaction and ethanolamine alone could be basic enough to stabilize the in situ generated selenium-containing species. In this respect, we propose that the present selenium-catalyzed carbonylation process could be self-promoted.

3. Conclusion

In summary, we have developed an efficient synthetic method for 2-oxazolidinones especially for chiral 2-oxazolidinones from 2-aminoethanols under very mild conditions. The catalytic system is simple. Both the catalyst and the solvent used can be easily recycled.



Scheme 1. Proposed pathway of the carbonylation reaction.

4. Experimental

4.1. General

2-Aminoethanols **1a–f**, elemental selenium (99.95%), carbon monoxide (99.9%), and all the organic solvents were all reagent grade and were used as received without further purification. 2-Aminoethanols **1h–j** were reduced from the corresponding amino acids according to the literature.[41] Melting points were determined on a Taike X-4 apparatus (Beijing, China) and were uncorrected.

4.2. A typical procedure for the synthesis of 2-oxazolidinone from ethanolamine and carbon monoxide catalyzed by selenium

Ethanolamine (10 mmol, 0.61 g) was dissolved in 10 ml of CH_3CN to which was added 0.5 mmol (0.0395 g) of elemental selenium, and carbon monoxide was bubbled into the solution at a rate of 12 ml/min for about 15 min at 30 °C (ambient temperature) until the gray selenium was dissolved completely. Then oxygen gas was passed through the solution in about 12% volume of carbon monoxide for 8 h. Finally the carbon monoxide stream was stopped while oxygen was continued to recover the selenium. Filtration of the selenium followed by removal the solvent gave the crude 2-oxazolidinone stoichiometrically. Further purification by short-column chromatography (silica gel, AcOEt) afforded **2a** in 93% (0.81 g) yield as a white solid; ^{1}H NMR (DMSO-d_6) δ 3.45 (q, 2H), 4.30 (t, 2H), 7.45 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 39.9, 64.2, 159.7.

4.2.1. 4,4-Dimethyl-2-oxazolidinone (2b). Purified by short-column chromatography (petroleum ether/AcOEt, 1:1); ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 6H), 4.08 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 27.1, 54.9, 76.7, 159.0.

4.2.2. 5-Methyl-2-oxazolidinone (2c). Purified by short-column chromatography (petroleum ether/AcOEt, 1:1); ^{1}H NMR (DMSO-d_6) δ 1.30 (d, 3H), 3.03 (t, 1H), 3.56 (m, 1H), 4.64 (m, 1H), 7.38 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 20.5, 46.5, 72.3, 159.0.

4.2.3. 4-Ethyl-2-oxazolidinone (2d). Purified by short-column chromatography (petroleum ether/AcOEt, 5:3); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H), 1.58 (m, 2H), 3.84 (m, 1H), 4.01 (t, 1H), 4.48 (t, 1H), 7.33 (br, 1H). ^{13}C NMR ($CDCl_3$) δ 8.4, 27.4, 53.1, 69.3, 159.9.

4.2.4. 4-Phenyl-2-oxazolidinone (2e). Purified by recrystallization from petroleum ether and acetone; ^{1}H NMR (DMSO-d_6) δ 4.00 (t, 1H), 4.67 (t, 1H), 4.94 (t, 1H), 7.31–7.42 (m, 5H), 8.23 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 55.3, 71.6, 126.2, 128.2, 128.9, 141.1, 159.2; (>99% ee).

4.2.5. 4-Methyl-2-oxazolidinone (2f). Purified by short-column chromatography (petroleum ether/AcOEt, 1:1); ^{1}H NMR (DMSO-d_6) δ 1.17 (q, 3H), 3.83–3.94 (m, 2H), 4.41 (m, 1H), 7.68 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 20.2, 47.1, 70.2, 158.4.

4.2.6. 4-Benzyl-2-oxazolidinone (2g). Purified by short-column chromatography (petroleum ether/AcOEt); ^{1}H NMR (DMSO-d_6) δ 2.72–2.85 (m, 2H), 3.97–4.05 (m, 2H), 4.25 (t, 1H), 7.24–7.33 (m, 5H), 7.82 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 40.3, 52.5, 52.6, 68.1, 126.7, 128.5, 129.5, 136.6, 158.8; (>99% ee).

4.2.7. 4-Isopropyl-2-oxazolidinone (2h). Purified by short-column chromatography (petroleum ether/AcOEt, 5:3) followed by recrystallization from petroleum ether; ^{1}H NMR (DMSO-d_6) δ 0.80–0.86 (dd, 6H), 1.60 (m, 1H), 3.52 (m, 1H), 3.98 (q, 1H), 4.31 (t, 1H), 7.79 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 18.2, 18.3, 32.8, 57.9, 67.9, 159.7.

4.2.8. 4-Isobutyl-2-oxazolidinone (2i). Purified by short-column chromatography (petroleum ether/AcOEt, 5:1); ^{1}H NMR (DMSO-d_6) δ 0.92 (m, 6H), 1.31 (m, 1H), 1.43 (m, 1H), 1.67 (m, 1H), 3.83–3.92 (m, 2H), 4.42 (m, 1H), 7.78 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 21.6, 22.6, 23.8, 43.9, 49.6, 69.2, 158.4.

4.2.9. 4-(2-Methylsulfanyl-ethyl)-2-oxazolidinone (2j). Purified by short-column chromatography (petroleum ether/AcOEt, 5:3); ^{1}H NMR (DMSO-d_6) δ 1.71 (m, 2H), 2.01 (s, 3H), 2.46 (m, 2H), 3.81–3.96 (m, 2H), 4.38 (t, 1H), 7.79 (br, 1H). ^{13}C NMR (DMSO-d_6) δ 15.3, 29.6, 35.1, 51.6, 69.6, 159.4; (>99% ee).

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