Upgrading CO_2 by incorporation into urethanes through silver-catalyzed one-pot stepwise amidation reaction

Qing-Wen Song,[a] Ping Liu,[a] Li-Hua Han,[a] Kan Zhang[a]* and Liang-Nian He[b]*

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, P. R. China

[b] State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China

One-pot two-step stepwise reaction of terminal propargylic alcohols, carbon dioxide, and primary/secondary amines for the effective synthesis of various urethanes through robust silver-catalysed C–O/C–N bond formation is reported. Catalytic activities were investigated by controlling catalyst loading, reaction pressure and time, and very high turnover number (turnover frequency) was obtained: 3350 (35 h^{-1}) with 0.01 mol% silver catalyst under 0.1 MPa, and up to 13360 (139 h^{-1}) with 0.005 mol% silver catalyst under 2.0 MPa at room temperature. The strategy was ingeniously regulated, and synchronously afforded a wide range of β-oxopropylcarbamate and 1,3-oxazolidin-2-one motifs in excellent yields and selectivity together with unprecedented high TON and TOF value.

Keywords Carbon dioxide utilization, Homogeneous catalysis, C-N bond formation, Silver catalysis, Synthetic method

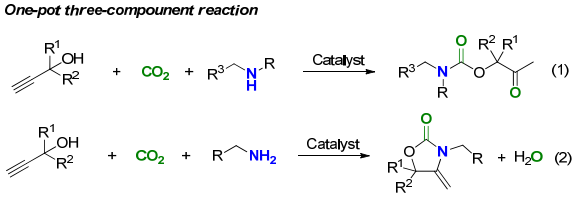
Introduction

Over the last several decades, the chemical utilization of the abundant, easily available, and renewable CO_2 feedstock as an integral part of the carbon cycle for producing chemicals, polymers, and fuels has received considerable attention.[1-3] Although CO_2 is thermodynamic stability and kinetic inertness, recent progress in the catalytic conversion of CO_2 has been remarkable. In ideal process, chemical fixation of CO_2 as green carbonyl source is of great significance as an alternative to the CO and phosgene process for the synthesis of valuable products, such as urea and its derivatives, urethanes, and polyurethanes through C-N bond formation.[4] In this respect, urethanes, among the most important carbonyl compounds such as *β*-oxopropylcarbamate and 1,3-oxazolidin-2-one motifs, are playing a significant role in organic synthesis and pharmaceutical chemistry.[5-10]

Various catalysts/promoters have been developed to allow the effective synthesis of urethanes from commercial propargylic alcohols, primary/secondary amines, and CO_2, including transition metal complexes (Ru,[11,12] Fe,[13] Cu,[14-17] Ag,[18-21] and La[22]) and organocatalysts (organic base[23,24] and ionic liquid[25]). In these systems, transition metal catalysis has more advantages such as using lower catalytic loading, higher effeciency and selectivity with mild reaction conditions than metal-free systems. Despite considerable progress has been made in the past few decades, converting CO_2 into readily useful chemicals still remains a daunting challenge presumably due to some limitations such as catalyst compatibility, harsh reaction conditions, low yields or selectivity. Therefore, development of effective methodologies with high turnover number (TON) and turnover frequency (TOF) for breaking through the bottleneck in the amidation reaction using CO_2 as a feedstock under mild conditions could be still highly desirable; this represents a significant and challenging area in both catalysis and sustainable chemistry.

As is well-known, *α*-alkylidene cyclic carbonates, generally synthesized through carboxylative cyclization of propargylic alcohols and CO_2, are key intermediate for the synthesis of *β*-oxopropylcarbamate and 1,3-oxazolidin-2-one motifs in the three-component reaction of propargylic alcohols, amines, and CO_2 (Scheme 1).

Scheme 1 Chemical fixation of CO_2 with propargylic alcohols and amines.



Although it is thermodynamic favorable and effective for carboxylative cyclization and the reaction of *α*-alkylidene cyclic carbonate with aliphatic amine, it is of much difficulty for the one-pot three-component reaction of propargylic alcohols, amines, and CO_2 to go smoothly with superior efficiency. Study revealed that active center of transition metal catalyst is prone to be restrained or poisoned by the electron-rich substrates such as amines which lead to a decreased catalytic performance and increased catalytic loading. Considering the limitation of the convenient routes and mechanism exploration in previous study, herein we became

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/cjoc.201700572

interested in developing an efficacious methodology for the conversion of CO_2 into valuable chemicals with great enhanced efficiency on three-component reaction. In this context, we hypothesized that one-pot stepwise strategy namely α-alkylidene cyclic carbonates can be efficiently produced in the first step as reactive intermediate through carboxylative cyclization of propargylic alcohols with CO_2, and subsequently amines are introduced with the generation of aimed compounds. Based on our knowledge in the area of CO_2 chemistry associated with propargylic alcohols,[11-25] we herein present a favorable one-pot stepwise process to synthesize β-oxopropylcarbamate and oxazolidinone scaffolds from terminal propargylic alcohols, CO_2, and amines. As a result, high effeciency with unprecedented TON and TOF values of the cascade three-component reaction under low catalytic loading of silver catalyst was obtained.

Experimental

Unless otherwise noted, carbon dioxide (99.999%), commercially available propargylic alcohols and amines. All starting materials were obtained from Aladdin and Alfa Aesar, and used as received. All reactions were carried out without any special precautions against air. ^{1}H NMR spectra was recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to $CDCl_3$ (7.26 ppm). ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ (77.00 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a RTX-5MS capillary column at an ionization voltage of 70 eV. The data are given as mass units per charge (m/z). High resolution mass spectrometry was conducted using a Bruker microTOF-Q III by ESI technique.

General procedure for the synthesis of β-oxopropylcarbamates

Taking the reaction of 2-methylbut-3-yn-2-ol (**1a**), pyrrolidine, and CO_2 as an example: a 75 mL stainless steel reactor equipped with a stir bar was charged with Ag_2CO_3 (2.8 mg, 0.01 mol%), (p-$CH_3OC_6H_4)_3P$ (14.1 mg, 0.04 mol%), **1a** (8.41 g, 100 mmol), and $CHCl_3$ (2 mL). Next, the pressure was kept to 2 MPa CO_2. Then, the mixture was stirred at 25 °C for the desired time. Excessive CO_2 was carefully released after the reaction. Open the reactor, pyrrolidine (7.11 g, 100 mmol) was introduced, and subsequently stirred for another two hours. The residue was flushed with CH_3CN (5 mL), and detected by GC method immediately. Finally, the solvent was distilled off and the residue mixture was purified by silica gel column chromatography to get the β-oxopropylcarbamate **3a**. The structure of products was further identified by using NMR and GC-MS techniques, which are consistent with those reported in the literature.[20,21]

2-Methyl-3-oxobutan-2-yl pyrrolidine-1-carboxylate (**3a**) Colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.37 (m, 4H), 2.14 (s, 3H), 1.87 (m, 4H), 1.45 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.0, 153.8, 62.8, 46.0, 23.8, 23.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 199.15 (1), 157.15 (2), 156.20 (19), 100.15 (1), 99.15 (8), 98.15 (100).

2-Methyl-3-oxobutan-2-yl piperidine-1-carboxylate (**3b**) Light brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (m, 4H, 2N-CH_2), 2.11 (s, 3H, COCH_3), 1.59-1.49 (m, 6H, -CH_2CH_2CH_2-), 1.43 (s, 6H, 2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.5 (C=O), 154.0 (N-**C=O**), 82.7, 44.6, 25.6, 24.0, 23.4, 23.2 ppm. GC-MS (EI, 70 eV) m/z (%) = 213.15 (1), 171.15 (2), 170.20 (15), 129.15 (1), 128.15 (12), 114.15 (1), 113.15 (8), 112.15 (100), 69.10 (46).

2-Methyl-3-oxobutan-2-yl 2-methylpiperidine-1-carboxylate (**3c**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.42-4.36 (m, 1H), 3.94-3.90 (d, 1H), 2.91-2.85 (m, 1H), 2.10 (s, 3H), 1.67-1.32 (m, 6H), 1.44 (3H), 1.43 (3H), 1.16-1.14 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.8, 154.3, 82.8, 46.5, 39.0, 30.0, 25.6, 23.64, 23.57, 23.4, 18.4 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 213.10 (1), 212.10 (2), 184.10 (14), 142.10 (10), 126.10 (100), 84.10 (13), 83.10 (8), 55.10 (17). HRMS (ESI): $C_{12}H_{22}NO_3^+$ for $[M+H]^+$ calculated 228.1594, found 228.1614.

2-Methyl-3-oxobutan-2-yl 4-(hydroxymethyl)piperidine-1-carboxylate (**3d**) White solid powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.17-4.13 (2H), 3.51 (d, J = 6.4 Hz, 2H), 2.79 (br, OH), 2.12 (s, 3H, CH_3), 1.77-1.64 (m, 4H), 1.45 (s, 6H), 1.21-1.11 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.8, 154.2, 83.1, 67.4, 44.0, 38.6, 28.6, 23.6, 23.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 158.10 (5), 142.10 (100), 114.10 (10), 69.10 (10), 43.10 (22), 28.10 (26). HRMS (ESI): $C_{12}H_{22}NO_4^+$ for $[M+H]^+$ calculated 244.1543, found 244.1545.

2-Methyl-3-oxobutan-2-yl morpholine-4-carboxylate (**3e**) Orange solid. M.p. 75-77 °C ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.62 (t, J = 4.0 Hz, 4H), 3.43 (t, J = 20.0 Hz, 4H), 2.09 (s, 3H), 1.42 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.2, 154.0, 83.3, 66.5, 44.5, 43.6, 23.5, 23.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 215.10 (1), 173.15 (2), 172.15 (18), 115.15 (6), 114.15 (100), 71.10 (2), 70.10 (49), 69.10 (2).

2-Methyl-3-oxobutan-2-yl diethylcarbamate (**3f**) Straw yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.30-3.25 (q, 4H, CH_2), 2.12 (s, 3H), 1.45 (s, 6H), 1.14 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.7, 154.6, 82.8, 41.8, 41.6, 23.6, 23.4, 14.1, 13.5 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 202.15 (1), 159.20 (2), 158.20 (16), 102.15 (3), 101.15 (6), 100.20 (100), 72.10 (47).

2-Methyl-3-oxobutan-2-yl dibutylcarbamate (**3g**) Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.20 (t, 4H), 2.11 (s, 3H), 1.52-1.47 (m, 4H), 1.43 (s, 6H), 1.34-1.24 (m, 4H), 0.92 (6H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.7 (C=O), 155.0 (N-C=O), 82.8, 47.0, 46.7, 30.8, 30.1, 23.6, 23.3, 19.9, 13.8 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 258.25 (1), 215.20 (2), 214.20 (12), 173.20 (1), 172.20 (12), 157.20 (10), 156.20 (100), 101.15 (2), 100.15 (35), 88.10 (7), 87.15 (2), 86.15 (27), 85.10 (14).

2-Methyl-3-oxobutan-2-yl cyclohexyl(methyl)carbamate (**3h**) Colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (m, 1H), 2.78 (s, 3H), 2.11 (s, 3H), 1.79-1.75 (m, 2H), 1.65-1.62 (m, 2H), 1.44 (s, 6H), 1.36-1.30 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 207.7, 155.0, 82.9, 54.8, 30.1, 28.4, 25.6, 25.4, 23.7, 23.4 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 198.10 (25), 156.10 (15), 140.10 (100), 114.10 (14), 83.10 (98), 70.10 (16), 59.10 (19), 57.10 (19), 55.10 (21), 43.10 (17). HRMS (ESI): $C_{13}H_{24}NO_3^+$ for $[M+H]^+$ calculated 242.1751, found 242.1779.

1-Acetylcyclohexyl pyrrolidine-1-carboxylate (**3i**) Colourless solid. M.p. 62-63 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (2H), 3.36 (2H), 2.12 (3H), 2.06-2.03 (2H), 1.89 (4H), 1.67-1.57 (5H), 1.54-1.44 (2H), 1.23 (1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.3 (C=O), 153.4 (N-C=O), 84.0, 46.0, 45.9, 30.9, 25.6, 25.1, 24.8, 23.6, 21.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 196.15 (M^+-43, 15), 98.15 (100).

1-Acetylcyclohexyl piperidine-1-carboxylate (**3j**) Colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45-3.36 (4H), 2.06 (s, 3H), 2.01-1.98 (2H), 1.64-1.38 (m, 13H), 1.24-1.12 (1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.1 (C=O), 153.7 (N-C=O), 84.1, 45.2, 44.6, 30.8, 25.9, 25.0, 24.2, 23.4, 21.4 ppm. MS (EI, 70 eV) *m/z* (%) = 210.20 (12), 112.15 (100), 69.10 (27).

3-Methyl-2-oxopentan-3-yl pyrrolidine-1-carboxylate (**3k**) Straw yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.36 (4H), 2.13 (3H), 1.96-1.87 (5H), 1.72-1.63 (1H), 1.45 (s, 3H), 0.88 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 208.3(C=O), 153.4 (N-C=O), 84.0, 46.0, 45.9, 30.9, 25.6, 25.1, 24.8, 23.6, 21.3 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 170.15 (M^+-43, 17), 98.15 (100).

General procedure for the synthesis of 1,3-oxazolidin-2-ones

Taking the reaction of 2-methylbut-3-yn-2-ol (1a), n-butylamine, and CO_2 as an example: a 75 mL stainless steel reactor equipped with a stir bar was charged with Ag_2CO_3 (2.8 mg, 0.01 mol%), (p-$CH_3OC_6H_4$)$_3$P (14.1 mg, 0.04 mol%), 1a (8.41 g, 100 mmol), and $CHCl_3$ (2 mL). Next, the pressure was kept to 2 MPa CO_2. Then, the mixture was stirred at 25 °C for the desired time. Excessive CO_2 was carefully released after the reaction. Open the reactor, n-butylamine (7.31 g, 100 mmol), $PhCH_3$ (10 mL) and 2.0 g 4Å MS were introduced, and subsequently stirred for another two hours at 120 ºC. The residue was flushed with CH_3CN (5 mL) and filtrated, and detected by GC method. Finally, the solvent was distilled off and the residue mixture was purified by silica gel column chromatography to get the 1,3-oxazolidin-2-one 4a. The structure of products was further identified by using NMR and GC-MS techniques, which are consistent with those reported in the literature.[20]

3-Butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (**4a**) Orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.06 (d, J = 4.0 Hz, 1H), 3.97 (d, J = 4.0 Hz, 1H), 3.42 (t, J = 8.0 Hz, 2H), 1.61-1.53 (m, 2H), 1.48 (s, 6H), 1.37-1.28 (m, 2H), 0.92 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 155.6 (C=O), 150.9, 81.9, 79.0, 41.1, 28.3, 27.9, 19.9, 13.7 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 183 (M^+, 21), 168 (84), 128 (32), 97 (58), 96 (100), 84 (52), 82 (84).

3-Cyclohexyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (**4b**) White solid. M.p. 54-56 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.19 (d, J = 4.0 Hz, 1H), 3.97 (d, J = 4.0 Hz, 1H), 3.58-3.50 (m, 1H), 2.11-2.01 (m, 2H), 1.86-1.64 (m, 4H), 1.45 (s, 6H), 1.32-1.14 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 155.0 (C = O), 150.7, 81.1, 79.7, 53.7, 28.3, 27.9, 25.9, 25.1 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 209.20 (10), 194.20 (3), 129.15 (8), 128.20 (100), 127.20 (25), 85.15 (4), 84.15 (31), 83.15 (5), 68.10 (9), 67.10 (16).

3-Benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (**4c**) Orange-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.25 (m, 5H, Ar-H), 4.64 (s, 2H), 4.03 (d, J = 4.0 Hz, 1H), 3.96 (d, J = 2.4 Hz, 1H), 1.51 (s, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.8, 150.2, 135.2, 128.6, 127.6, 126.9, 82.2, 80.5, 45.0, 27.8 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 217.15 (M^+, 21), 172.20 (7), 91.10 (100).

3-Butyl-4-methylene-1-oxa-3-azaspiro[4.5]decan-2-one (**4d**) White solid. M.p. 60-62 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.04 (d, J = 4.0 Hz, 1H), 3.92 (d, 1H), 3.40 (t, J = 8.0 Hz, 2H), 1.83-1.30 (m, 14H), 0.90 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 155.8 (C=O), 150.8, 83.5, 79.2, 40.9, 36.8, 28.3, 24.6, 21.5, 19.8, 13.6 ppm. GC-MS (EI, 70 eV) *m/z* (%) = 223.20 (32), 181.20 (50), 168.20 (100), 137.20 (29), 136.20 (24), 112.10 (51), 95.15 (26), 67.10 (20).

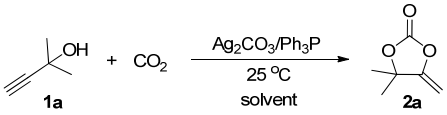
Results and discussion

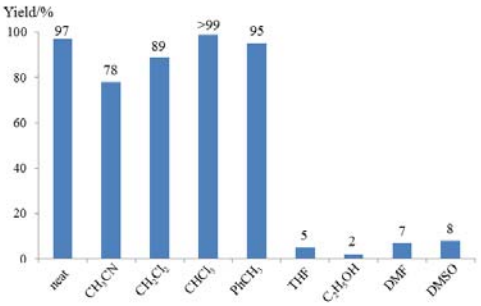
Initially, we explored the carboxylative cyclization of propargylic alcohols and CO_2 via robust silver catalysis to confirm the highest efficiency. As shown in Scheme 2, the reaction of **1a** and CO_2 with affording α-alkylidene cyclic carbonate (**2a**) disclosed distinct results in different medium. Despite unclear mechanism, we envisioned that solvent is of much importance to promote the formation of well-defined silver complex and stabilize it. In this protocol, almost quantitative yield of **2a** was obtained in trichloromethane at ambient conditions.

Subsequently, we further examined the catalytic activities of silver system with rich-electron phosphine ligand. The use of 0.05 mol% of Ag_2CO_3 in combination with PPh_3 resulted in 62% conversion of propargylic alcohol (**1a**) into the α-alkylidene cyclic carbonate (**2a**) after 12 hours, whereas using (p-$MeOC_6H_4$)$_3$P led to an increase yield but (p-MeC_6H_4)$_3$P show decrease trend as the yield (Table 1, entries 1-3). These results indicated that the phosphine ligand and substituent group in aromatic structure could both regulate the Lewis acidity of the silver ion and the steric configuration of silver complex for the effective activation and catalysis function. Therefore, the steric and electron effect of phosphine ligand are both the important factor for the catalytic activity of silver complex. However, PCy_3 and bidentate phosphine ligand such as

1,3-bis(diphenylphosphino)propane (Dppp) proved to be little effective under the given conditions, whereas Xantphos gave 44% **2a** yield, suggesting a crucial role of phosphine structure in promoting catalytic performance (Table 1, entries 4-6).

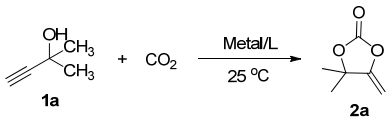
Scheme 2 Solvent investigation.

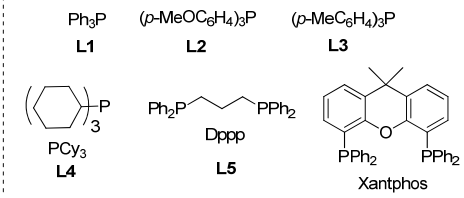




Reaction conditions: **1a** (0.421 g, 5 mmol), Ag_2CO_3 (6.9 mg, 0.5 mol%), PPh_3 (26.2 mg, 2 mol%), solvent (1 mL), CO_2 balloon, 2 h, 25 °C. Yield was determined by GC with biphenyl as the internal standard.

Table 1 Carboxylic cyclization of propargylic alcohols with CO_2[a]





Entry	Ligand	P (MPa)	T (°C)	t (h)	Yield (%)[b]	TON	TOF (h^{-1})
1	**L1**	balloon	25	12	62	1240	103
2	**L2**	balloon	25	12	65	1300	108
3	**L3**	balloon	25	12	44	880	73
4	**L4**	balloon	25	12	<1	-	-
5	**L5**	balloon	25	12	1	20	1
6	**L6**	balloon	25	12	26	520	43
7[c]	**L2**	balloon	25	12	84	1680	140
8[c]	**L2**	1.0	25	6	95	1906	318
9[c]	**L2**	2.0	25	6	98	1962	327
10[c]	**L2**	balloon	40	12	63	1260	105
11[c]	**L2**	balloon	60	12	3	60	5
12[c,d]	**L2**	balloon	25	48	17	1840	38
13[c,d]	**L2**	balloon	25	96	34	3350	35
14[c,e]	**L2**	2	25	96	31	12160	127
15[c,f]	**L2**	2	25	96	67	13360	139

[a]Reaction conditions: **1a** (1.6824 g, 20 mmol), Ag_2CO_3 (2.8 mg, 0.05 mol%), ligand (0.2 mol%), CO_2 balloon, 25 °C, 12 h. [b]Determined by GC with biphenyl as the internal standard. [c]$CHCl_3$ (2 mL). [d]**1a** (8.41 g, 100 mmol), Ag_2CO_3 (2.8 mg, 0.01 mol%), **L2** (14.1 mg, 0.04 mol%). [e]**1a** (33.64 g, 400 mmol), Ag_2CO_3 (2.8 mg, 0.0025 mol%), **L2** (14.1 mg, 0.01 mol%). [f]**1a** (16.82 g, 200 mmol), Ag_2CO_3 (2.8 mg, 0.005 mol%), **L2** (14.1 mg, 0.02 mol%). TON = **2a** (mol)/Ag_2CO_3 (mol); TOF = TON/time (hour).

Next, the survey of other reaction parameters was conducted using $(p\text{-}MeOC_6H_4)_3P$ as the ligand. Increase the pressure, the reaction ratio was greatly improved, and almost quantitative yield was obtained with high TON and TOF (Table 1, entries 7-9). The increase of CO_2 density contributes to the promotion of carboxylative cyclization of propargylic alcohols and CO_2 according to the Le Chartelier's principle. However, increase reaction temperature is not beneficial for the reaction probably due to the instability of silver complex in high temperature (entries 10 and 11). Under atmospheric pressure of CO_2, the TON value up to 3350 with the loading of 0.01 mol% Ag_2CO_3 for 96 h (entry 13). Furthermore, the TON value up to 13360 with the TOF value of 139 h^{-1} was gained through adjusting the catalyst usage (entry 15). In 2012, Nizuno group reported $(^nBu_4N)_2WO_4$ catalyzed carboxylative cyclization with TON value of up to 473 (TOF 20) which represented the

highest efficiency among the reported metal-free systems.[26] In our previous work, a robust catalytic system consisting of (^{n}C$_7$H$_{15}$)$_4$NBr and AgOAc was developed for the synthesis of *a*-alkylidene cyclic carbonates with unprecedentedly high turnover number up to 6024 (TOF 34) to date.[27] Through the comparison with these excellent catalytic systems, great advance in the work was made. Similarity, the two-step strategy also gave aimed urethanes with unprecedentedly high TON and TOF value in excellent selectivity. Notably, the continuously increased TON value (or yield) and the decreased TOF value with prolonging the reaction time (entries 7, 12-15) indicated that the catalyst still showed high activity even though a tendency to lower catalytic rate.

Notably, the reusability of silver complex in the carboxylic cyclization of propargylic alcohol with CO_2 was also demonstrated through a simple recycling method of homogeneous silver complex catalyst (Scheme S1, Supporting Information). The excellent results (Conv./Yield: >98%) revealed that the recovered catalyst still performed good catalytic activity after three runs (Scheme S2).

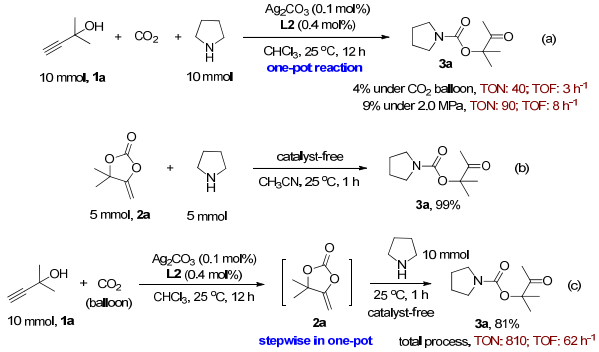
Generally, in many robust transition metal systems, inactive reaction atmosphere was required to guarantee the promotion of conversion.[28,29] Herein, several experiments under various reaction atmospheres were performed to investigate the tolerance. Under different gas atmosphere such as reducing, oxidizing and inert gas (Table 2, entries 1-5), the reaction was not inhibited in all of the cases. It is worth noting that the yield reduced with the decreasing of CO_2 content which further indicates the concentration of CO_2 is one of the most key parameters during the conversion.

Having established the highly effective silver-catalyzed carboxylative cyclization protocol, we then studied the new strategy for synthesis of *β*-oxopropylcarbamates through C-N bond formation. Initially, we performed the control experiments to compare the reactivity. In traditional three-component reaction of **1a**, pyrrolidine, and CO_2, only 4% *β*-oxopropylcarbamate (**3a**) yield under atmospheric pressure and 9% under 2 MPa were obtained (Scheme 3, a), although the excellent yield and selectivity of carboxylative cyclization of propargylic alcohols with CO_2, and amidation of **2a** with pyrrolidine (Scheme 3, b). Gratifyingly, **3a** was obtained in a yield of 81% with significant advantage in TON and TOF value by employing one-pot stepwise method under the same reaction conditions (Scheme 3, c). These results preliminary displayed the higher production of *β*-oxopropylcarbamates with higher TON and TOF value than that of traditional effective systems**.**

Table 2 Fixation of CO_2 under various gas atmosphere[a]

Entry	Gas	Initial	Yield	TON	TOF
	mixture	ratio	(%)[b]		(h^{-1})
1	H_2/CO_2	3:1	11.8	118	10
2	Ar/CO_2	4:1	7.0	70	6
3	N_2/CO_2	4:1	6.3	63	5
4	air/CO_2	9:1	4.6	46	4
5[c]	H_2/CO_2	3:1	19.9	199	17

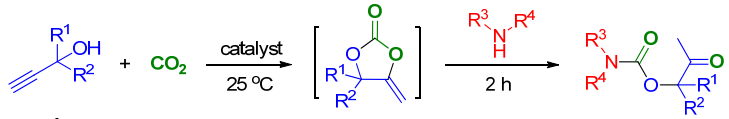
[a]Reactions were carried out with 10 mmol **1a**, 0.1 mol% Ag_2CO_3, 0.4 mol% **L2**, $CHCl_3$ (1 mL) under balloon (5 L) at 25 °C for 12 h. [b]Determined by GC with biphenyl as the internal standard. [c]Ag_2CO_3 (28 mg, 1 mol%), **L2** (141 mg, 4 mol%), $CHCl_3$ (2 mL).



Scheme 3 Control experiments.

With an optimized catalytic system in hand, we explored the scope of the three-component reaction by employing a variety of secondary amines and typical terminal propargylic alcohols under CO_2 atmosphere (Table 3). The one-pot stepwise reactions initially took place via the formation of *a*-methylene cyclic carbonates and a subsequent aminolysis sequence. During the procedure, no isolation process for the carbonate intermediate was needed and the catalytic activity of silver complex was also kept well without any inhibition by introducing secondary amines separately. Various representative *β*-oxopropylcarbamates synthesized are depicted in Scheme 3. Under atmospheric pressure of CO_2, the yield was up to 32.7% and TON value of up to 3270 at a catalytic loading of 0.01 mol% at room temperature for 96 h (entries 1 and 6). Under the same conditions, the reaction was proceeded smoothly to give good yield and TON value. Both cyclic and linear aliphatic secondary aliphatic amines afforded the corresponding product with moderate to excellent yields. As seen from the results, when increasing the steric hindrance of substrate such as 2-methylpiperidine and n-dibutylamine, the reactive activity slightly declined (entries 3 and 7). In addition, electronic effect is also one of the most important factors to influence the reactivity of amines such as 1-oxa-4-azacyclohexane and N-methylbenzylamine (entries 5 and 8).

Table 3 Scope of the reaction of propargylic alcohols, CO_2, and secondary amines[a]



Entry	Product **3**	Yield (%)[b]	TON	TOF (h^{-1})	Entry	Product **3**	Yield (%)[b]	TON	TOF (h^{-1})
		32.7[c]	3270	34			30.5[c]	3050	31
		92.4	9240	96	6	**3f**	91.2	9120	93
1	**3a**	60.8[d]	11200	117	7	**3g**	56.0	5600	57
		26.8[e]	10720	112	8	**3h**	64.5	6450	66
2	**3b**	91.8	9180	94	9	**3i**	92.6	9260	94
3	**3c**	37.7	3770	38	10	**3j**	93.2	9320	95
4	**3d**	90.4	9040	92	11	**3k**	60.8	6080	62
5	**3e**	77.4	7740	79					

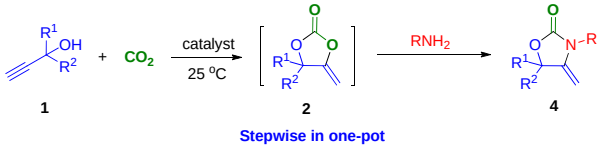
[a]Unless otherwise specified, the reactions in first step were performed with **1a** (8.41 g, 100 mmol), Ag_2CO_3 (2.8 mg, 0.01 mol%), **L2** (14.1 mg, 0.04 mol%), 2.0 MPa, $CHCl_3$ (2 mL), 96 h, 25 °C; reaction conditions in second step were performed with equivalent amines at ambient temperature for 2 h. [b]Determined by GC with biphenyl as the internal standard. [c]CO_2 balloon. [d]**1a** (16.82 g, 200 mmol), Ag_2CO_3 (2.8 mg, 0.005 mol%), **L2** (14.1 mg, 0.02 mol%). [e]**1a** (33.64 g, 400 mmol), Ag_2CO_3 (2.8 mg, 0.0025 mol%), **L2** (14.1 mg, 0.01 mol%).

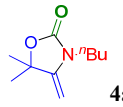
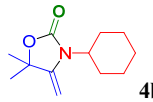
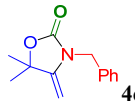
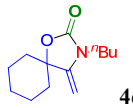
Totally, the steric hindrance and electronic induction effect reduced the nucleophilicity of amines, which further depressed the activity of nucleophilic substrates. For piperidin-4-ylmethanol bearing with two type functional group, target product was obtained with excellent selectivity (entry 4).

Typical terminal propargylic alcohols with alkyl substituents at the propargylic position (**1b** and **1c**) underwent the reaction smoothly under the identical reaction conditions to afford the corresponding *β*-oxopropylcarbamates (**3i-k**) in yields of 60.8%-93.2% and TON value of up to 9320. Additionally, **1c** also showed a good reactivity in high yield and TON value.

The successful transformation of propargylic alcohols and secondary amines to *β*-oxopropylcarbamates with high efficiency through CO_2 fixation under extremely mild conditions prompted us to expand potential applications of this one-pot stepwise reaction strategy to the synthesis of 1,3-oxazolidin-2-one motifs via the three-component reaction of propargylic alcohols, primary amines and CO_2 under mild conditions as listed in Table 4.

Table 4 Scope of the reaction of propargylic alcohols, CO_2, and primary amines[a]

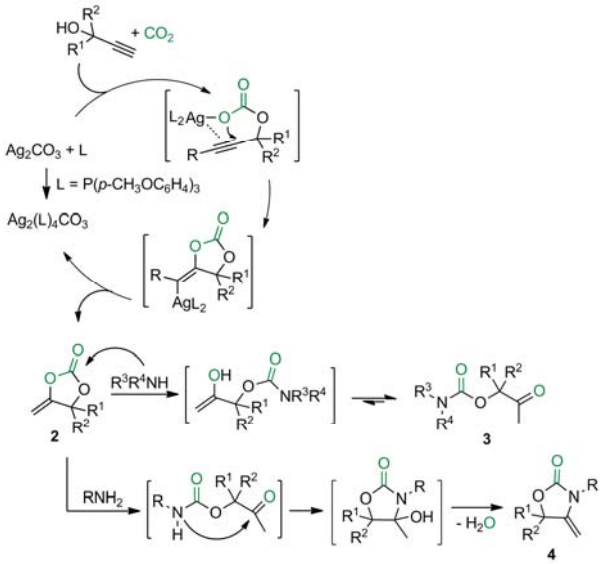


Entry	Product **4**	Yield (%)[b]	TON	TOF (h^{-1})
1	 **4a**	92.5	9250	94
2	 **4b**	89.4	8940	91
3	 **4c**	88.3	8830	90
4	 **4d**	89.3	8930	91

[a]Unless otherwise specified, the reactions in first step were performed with **1a** (8.41 g, 100 mmol), Ag_2CO_3 (2.8 mg, 0.01 mol%), **L2** (14.1 mg, 0.04 mol%), 2.0 MPa, $CHCl_3$ (2 mL), 96 h, 25 °C; reaction conditions in second step were performed with equivalent amines, 10 mL $PhCH_3$ and 2.0 g 4Å MS at 120 °C for 2 h. [b]Determined by GC with biphenyl as the internal standard.

Pleasingly, the transformation was performed smoothly with the catalysis of low loading silver catalyst. Herein, the reflux conditions of toluene were used with the assistance of 4Å molecular sieve for removing the water generated from intramolecular dehydration. When **1a** was used, and amines bearing n-butyl, cyclohexyl, and benzyl groups, respectively, were subjected to the reaction conditions, the 1,3-oxazolidin-2-one derivatives (**4a–4c**) were obtained in excellent yields. Furthermore, reaction of propargylic alcohols with cyclohexyl substituent gave the desired products **4d** smoothly.

A plausible reaction mechanism is proposed as shown in Scheme 4. Initially, the carboxylative cyclization of propargylic alcohol with CO_2 affords the α-alkylidene cyclic carbonate intermediate through *in situ* formed silver complex catalysis,[4] which then goes through a nucleophilic ring-opening reaction after introducing secondary amines to generate the corresponding *β*-oxopropylcarbamates **3**. Additionally, when primary amines are employed, the carbamate intermediate can further take place intramolecular nucleophilic ring-closing reaction and elimination reaction with the generation of oxazolidinones **4**.



Scheme 4 Plausible mechanism.

Conclusions

In summary, a successful protocol of one-pot stepwise three-component reaction of propargylic alcohols, carbon dioxide, and primary/secondary amines is disclosed for the effective synthesis of various urethanes with excellent TON value of up to 11,200 and TOF of up to 117 h^{-1} at mild reaction conditions. The overwhelming superiority of the stepwise strategy is verified in comparison with the traditional one-pot method. This approach also does not require high loading of silver catalyst, high pressure and temperature, and no intermediate was required to be isolated. Notably, the good reusability of silver complex is demonstrated, and the simple recycling method of homogeneous catalyst is well developed. Finally, a broad amine substrate application scope is been primarily demonstrated.

Acknowledgement

We are grateful to the National Natural Science Foundation of China (21602232), the Natural Science Foundation for Youths of Shanxi (201701D221057), and Project of "Utilization of Low Rank Coal" Strategic Leading Special Fund, Chinese Academy of Sciences (XDA-07070800, XDA-07070400).

References

1 Aresta, M.; Dibenedetto, A.; Angelini A. *Chem. Rev.* **2014**, *114*, 1709−1742.
2 He, M.; Sun, Y.; Han, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 9620−9633.
3 Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.
4 Yang, Z.-Z.; He, L.-N.; Gao, J.; Liu, A.-H.; Yu, B. *Energy Environ. Sci.* **2012**, *5*, 6602–6639.
5 Adams, P.; Baron, F. A. *Chem. Rev.* **1965**, *65*, 567–602.
6 Greene, T. W.; Wuts, P. G. M. Protective Groups in Organic

Synthesis, 2nd ed., Wiley, New York, **1999**, 315–348.
7 Roers, R.; Verdine, G. L. *Tetrahedron Lett.* **2001**, *42*, 3563–3565.
8 Leroux, M. L.; Le Gall, T.; Mioskowski, C. *Tetrahedron Asymmetry* **2001**, *12*, 1817–1823.
9 Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238–1256.
10 Vara Prasad, J. V. N. *Curr. Opin. Microbiol.* **2007**, *10*, 454–460.
11 Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1987**, *28*, 2005–2008.
12 Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 4389–4391.
13 Kim, T. J.; Kwon, K. H.; Kwon, S. C.; Baeg, J. O.; Shim, S. C. *J. Organomet. Chem.* **1990**, *389*, 205–217.
14 Kim, H. S.; Kim, J. W.; Kwon, S. C.; Shim, S. C.; Kim, T. J. *J. Organomet. Chem.* **1997**, *545–546*, 337–344.
15 Kwon, S. C.; Cho, C. S.; Shim, S. C.; Kim, T. J. *Bull. Korean Chem. Soc.* **1999**, *20*, 103–105.
16 Gu, Y.-L.; Zhang, Q.-H.; Duan, Z.-Y.; Zhang, J.; Zhang, S.-G.; Deng, Y.-Q. *J. Org. Chem.* **2005**, *70*, 7376–7380.
17 Jiang, H.-F.; Zhao, J.-W.; Wang, A-Z. *Synthesis* **2008**, 763–769.
18 Qi, C.-R.; Huang, L.-B.; Jiang, H.-F. *Synthesis* **2010**, 1433–1440.
19 Jiang, H.-F.; Zhao, J.-W. *Tetrahedron Lett.* **2009**, *50*, 60–62.
20 Song, Q.-W.; Yu, B.; Li, X.-D.; Ma, R.; Diao, Z.-F.; Li, R.-G.; Li, W.; He, L.-N. *Green Chem.* **2014**, *16*, 1633–1638.
21 Song, Q.-W.; Chen, W.-Q.; Ma, R.; Yu, A.; Li, Q.-Y.; Chang, Y.; He, L.-N. *ChemSusChem* **2015**, *8*, 821–827.
22 Shim, S. C.; Baeg, J. O.; Doh, C. H.; Youn, Y. Z.; Kim, T. J. *Bull. Korean Chem. Soc.* **1990**, *11*, 467–468.
23 Qi, C.-R.; Jiang, H.-F. *Green Chem.* **2007**, *9*, 1284–1286.
24 Della Ca', N.; Gabriele, B.; Ruffolo, G.; Veltri, L.; Zanetta, T.; Costa, M. *Adv. Synth. Catal.* **2011**, *353*, 133–146.
25 Zhang, Q.-H.; Shi, F.; Gu, Y.-L.; Yang, J.; Deng, Y.-Q. *Tetrahedron Lett.* **2005**, *46*, 5907–5911.
26 Kimura, T.; Kamata, K.; Mizuno N. *Angew. Chem. Int. Ed.* **2012**, *51*, 6700–6703.
27 Song, Q.-W.; He, L.-N. *Adv. Synth. Catal.* **2016**, *358*, 1251–1258.
28 Yu, D.; Teong, S. P.; Zhang, Y. *Coord. Chem. Rev.* **2015**, *293–294*, 279–291.
29 Huang, K.; Sun, C.-L.; Shi, Z.-J. *Chem. Soc. Rev.* **2011**, *40*, 2435–2452.

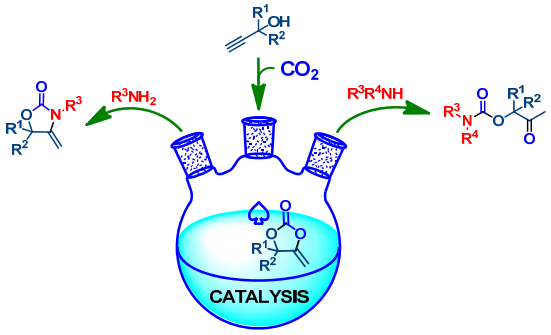
(Manuscript No. Editor) ((will be filled in by the editorial staff))

Entry for the Table of Contents

Page No.

Upgrading CO_2 by incorporation into urethanes through silver-catalyzed one-pot stepwise amidation reaction

Qing-Wen Song; Ping Liu; Li-Hua Han; Kan Zhang;* Liang-Nian He*



One-pot two-step procedure fixation of CO_2 for urethanes synthesis with unprecedented TON and TOF value through silver catalysis was described.