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Silver-catalyzed activation of internal propargylic alcohols in supercritical carbon dioxide: efficient and eco-friendly synthesis of 4-alkylidene-1,3-oxazolidin-2-ones

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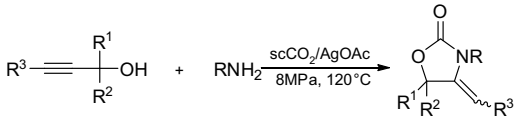
ABSTRACT

The silver-catalyzed cycloaddition reactions of carbon dioxide with internal propargylic alcohols and primary amines under supercritical conditions give 4-alkylene-1,3-oxazolidin-2-ones in good to excellent yields. The optimized conditions are to use an alcohol (2 mmol), an amine (2 mmol), silver acetate (0.1 mmol), and carbon dioxide (8 MPa) at 120 °C.

Carbon dioxide is a major greenhouse gas, and a great deal of carbon dioxide has been ceaselessly emitted into atmosphere from burning fossil fuel. The issue on recycling or removing CO_2 from industrial emissions has attracted increased attentions. On the other hand, carbon dioxide is an abundant, cheap, and nontoxic biorenewable resource, could potentially be an attractive raw material to replace toxic chemicals such as phosgene, isocyanates, or CO.[1]

Oxazolidinones are useful heterocyclic compounds in organic synthesis. They have a wide range of applications in asymmetric syntheses as chiral synthons or chiral auxiliaries,[2] and in medicinal chemistry because of their good antibacterial properties.[2a,3] A number of procedures to synthesize 4-methylene-1,3-oxazolidin-2-ones have been developed, while few processes to produce 4-substituted methylene ones have been reported.[4,5] Schmalz et al. reported that 4-alkylidene-1,3-oxazolidin-2-ones were prepared from *o*-propargyl carbamates under catalysis of AuCl in MeCN,[6] and Chandrasekaran's group disclosed that *o*-propargyl carbamates were transformed into 4-alkylidene-1,3-oxazolidin-2-ones catalyzed by base in DMF.[7] However, the employed *o*-propargyl carbamates are very expensive and not easily available, and volatile organic chemicals (VOCs) are used. It was reported that terminal propargylic alcohols smoothly reacted with carbon dioxide to produce 4-methylene-1,3-oxazolidin-2-ones.[5] However, the cycloaddition of internal propargylic alcohols with CO_2 and amine has not been reported. Recently, we found that internal propargylic alcohols could be activated to form oxazolidinones in the presence of silver salts in supercritical carbon dioxide (Scheme 1).

We first examined the cycloaddition reaction of 3-ethyl-1-phenyl-1-heptyn-3-ol (**1a**) and *n*-butylamine (**2a**) in $scCO_2$ under different reaction conditions, and the results are summarized in Table 1. CuI did not catalyze the reaction of internal propargylic



1

1a: R^1 = *n*-Bu, R^2 = Et, R^3 = Ph
1b: R^1, R^2 = -C_5H_{10}-, R^3 = Ph
1c: R^1, R^2 = -C_5H_{10}-, R^3 = Me
1d: R^1 = H, R^2 = H, R^3 = Ph
1e: R^1 = H, R^2 = H, R^3 = Me
1f: R^1 = H, R^2 = Me, R^3 = Ph
1g: R^1 = H, R^2 = Et, R^3 = Et

2

2a: R = *n*-Bu
2b: R = *s*-Bu
2c: R = Allyl
2d: R = Cy
2e: R = *n*-C_6H_{13}

3

Scheme 1. Cycloaddition reaction of internal propargylic alcohols with primary amines in $scCO_2$.

Table 1
Optimizing the reaction conditions for the cycloaddition of internal propargylic alcohols with amines in $scCO_2$[a]

Entry	Catalyst	Temperature (°C)	Pressure (MPa)	Yield[b] (%)
1	CuI	140	12	0
2	CuI/CNT	140	12	49
3	$AgBF_4$	140	12	94
4	AgOAc	140	12	93
5	Ag_2CO_3	140	12	93
6	AgOAc	120	12	92
7	AgOAc	100	12	79
8	AgOAc	120	10	97
9	AgOAc	120	8	98
10	AgOAc	120	6	51

[a] Reaction conditions: **1a** (2 mmol), **2a** (2 mmol), cat. (0.1 mmol), 24 h.
[b] Determined by GC analysis.

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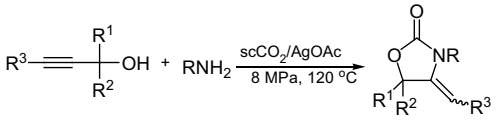
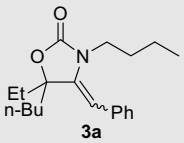
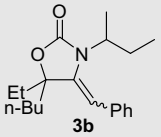
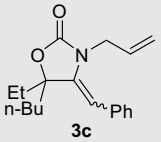
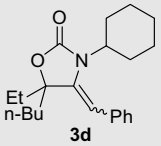
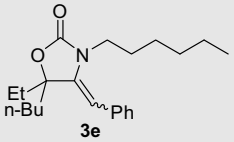
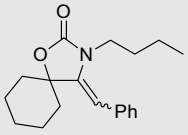
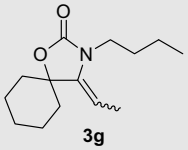
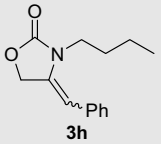
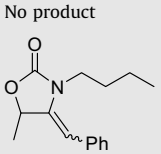
Table 2
Silver acetate-catalyzed cycloaddition reaction of internal propargylic alcohols with primary amines in $scCO_2$[a]



1 2 3

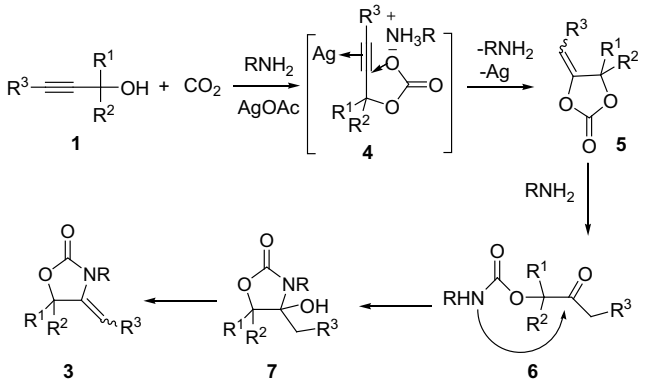
Entry	Alcohol	Amine	Product	*Z*:*E*[b]	Yield[c] (%)
1	**1a**	**2a**	 **3a**	50:50	95
2	**1a**	**2b**	 **3b**	50:50	93
3	**1a**	**2c**	 **3c**	55:45	90
4	**1a**	**2d**	 **3d**	55:45	85
5	**1a**	**2e**	 **3e**	50:50	97
6	**1b**	**2a**	 **3f**	55:45	96
7	**1c**	**2a**	 **3g**	90:10	91
8	**1d**	**2a**	 **3h**	70:30	73
9	**1e**	**2a**	No product	—	0[d]
10	**1f**	**2a**	 **3i**	80:20	80
11	**1g**	**2a**	No product	—	0[e]

[a] Reagents and conditions: alcohol **1** (2 mmol), amine **2** (2 mmol), AgOAc (0.1 mmol), Pco_2 = 8 MPa, 120 °C.
[b] Isolated yield.
[c] Determined by GC.
[d] **1e** Remained unchanged.
[e] **1g** Remained unchanged.

alcohols with carbon dioxide and primary amine, which differed from that of terminal propargylic alcohols (Table 1, entry 1).[5a] Even though CuI was supported on carbon nanotube, it did not drive the reaction satisfactorily (entry 2). When $AgBF_4$ was added in the reaction system, it was exciting that 4-benzylidene-3,5-dibutyl-5-ethyloxazolidin-2-one (**3a**) was obtained in 94% yield (entry 3). The further experiments showed that the counter ion of the silver salt had little effect on the reaction (entries 4, 5). When the temperature was reduced from 120 to 100 °C, the yield diminished from 92% to 79% (entries 6, 7). The pressure of 8 MPa might be the most suitable one as the highest yield was achieved (98%) (entries 6, 8–10). Therefore, the best reaction conditions were 3-ethyl-1-phenyl-1-heptyn-3-ol (2 mmol), *n*-butylamine (2 mmol), and silver acetate (0.1 mmol); CO_2 pressure, 8 MPa; temperature, 120 °C; time, 24 h.

As seen in Table 2, a series of primary amines such as *n*-butylamine (**2a**), *s*-butylamine (**2b**), allylamine (**2c**), cyclohexylamine (**2d**), and *n*-hexylamine (**2e**) were employed to go across the cycloaddition reaction with 3-ethyl-1-phenylhept-1-yn-3-ol (**1a**) in $scCO_2$, and the corresponding 4-alkylidene-1,3-oxazolidin-2-ones were obtained in 95%, 93%, 90%, 85%, and 97% isolated yields, respectively (Table 2, entries 1–5).[8] Then, various internal propargylic alcohols were chosen to react with *n*-butylamine (**2a**) in $scCO_2$. 1-(Phenylethynyl)cyclohexanol (**1b**) and 1-(prop-1-ynyl)cyclohexanol (**1c**) proceeded smoothly to give the desired products in 96% and 91% yields (entries 6, 7). It was noteworthy that primary internal propargylic alcohol 3-phenylprop-2-yn-1-ol (**1d**) and secondary internal propargylic alcohol 4-phenylbut-3-yn-2-ol (**1f**) could smoothly react to produce 4-alkylidene-1,3-oxazolidin-2-ones in 73% and 80% yields (entries 8, 10). These results did not coincide with those in our previous work.[4a] We considered that these products with exocyclic double bonds other than endocyclic ones were formed because the newly formed double bonds could conjugate with benzene rings. However, internal propargylic alcohols with α-hydrogen whose R^3 was alkyl, such as but-2-yn-1-ol (**1e**) and hept-4-yn-3-ol (**1g**), did not undergo the cycloaddition reaction (entries 9, 11).

In comparison with terminal propargylic alcohols,[4a,9] internal propargylic ones needed more active catalyst, such as silver acetate, and higher reaction temperature. This indicated that the internal propargylic alcohols were less reactive than terminal ones. A proposed mechanism for the cycloaddition of internal propargylic alcohols with amines in $scCO_2$ is shown in Scheme 2. Ag salt could promote the cycloaddition reaction of inert internal propargylic alcohol and CO_2 to form α-alkylene cyclic carbonate **5**. The nucleophilic addition of primary amine to **5** could afford 2-oxoalkylcarbamate **6**. 4-Hydroxy cyclic carbamate **7**, a reaction



Scheme 2. Proposed mechanism for cycloaddition reaction of internal propargylic alcohols with primary amines.

intermediate formed via the intramolecular cyclization of **6**, could be alternatively eliminated, and *Z*/*E* ratio in the products almost rested with stochastic process.

In conclusion, we have shown that internal propargylic alcohols can be activated for the cycloaddition reaction with primary amines and carbon dioxide under supercritical condition catalyzed by silver salt to afford 4-alkylidene-1,3-oxazolidin-2-ones. Other efficient chemical fixations of carbon dioxide into useful fine chemicals are explored in our laboratory.

Acknowledgments

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8. A 15 mL polytetrafluoroethylene (PTFE) reaction vessel was charged with catalyst (0.1 mmol), internal propargylic alcohol (2 mmol), and amine (2 mmol). The vessel was fixed into a stainless autoclave in a pressure regulating system. The autoclave was sealed. Liquid carbon dioxide was introduced from a cylinder, and it reacted at the selected temperature under magnetic stir for the required reaction time. When the reaction was completed, the vessel was cooled with an ice-bath, and the pressure was released slowly to atmospheric pressure. The residual was flushed with 3×10 mL diethyl ether. The products were purified by column chromatography (gel, petroleum ether/ethyl acetate, 6:1), and were characterized by ^{1}H NMR, ^{13}C NMR, and MS. *4-Benzylidene-3,5-dibutyl-5-ethyloxazolidin-2-one* (**3a**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2959, 2929, 2873, 1768, 1672; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.82–0.86 (m, 3H), 0.94–0.98 (m, 6H), 1.34–1.40 (m, 6H), 1.62–1.64 (m, 6H), 3.26–3.30 (t, J = 7.6 Hz, 2H), [3.50–3.56 (t, J = 7.4 Hz, 2H)], 5.40 (s, 1H), [5.79 (s, 1H)], 7.12–7.17 (m, 3H), 7.24–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 7.1, 13.3, 13.9, 20.1, 22.4, 24.8, 28.9, 31.9, 38.4, 41.1, 88.4, 99.0, 127.0, 127.8, 128.1, 129.3, 129.7, 134.9, 140.5, 157.2; MS (EI, 70 eV): m/z (%) = 315 [M$^+$] (32), 259 (100), 244 (22), 224 (21), 202 (32), 180 (25), 145 (8), 117 (15), 91 (16), 57 (8), 41 (5). *4-Benzylidene-3-sec-butyl-5-butyl-5-ethyloxazolidin-2-one* (**3b**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2968, 2934, 2875, 1760, 1666; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.85–0.89 (m, 3H), 0.94–0.99 (m, 6H), 1.36–1.45 (m, 7H), 1.63–1.69 (m, 6H), 3.42–3.46 (t, J = 7.6 Hz, 1H), [3.91–3.95 (t, J = 7.8 Hz, 1H)], 5.32 (s, 1H), [5.94 (s, 1H)], 7.12–7.18 (m, 3H), 7.25–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 6.3, 10.4, 13.0, 16.0, 21.5, 23.8, 24.9, 31.1, 37.8, 50.6, 86.5, 98.5, 126.1, 127.1, 128.4, 134.3, 139.8, 154.9; MS (EI, 70 eV): m/z (%) = 315 [M$^+$] (32), 259 (100), 244 (22), 224 (21), 202 (32), 180 (25), 145 (8), 117 (15), 91 (16), 57 (8), 41 (5). *3-Allyl-4-benzylidene-5-butyl-5-ethyloxazolidin-2-one* (**3c**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2959, 2931, 2873, 1742, 1673; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.89–0.93 (m, 3H), 0.95–0.98 (m, 3H), 1.34–1.38 (m, 4H), 1.62–1.70 (m, 3H), 3.93–3.97 (t, J = 7.8 Hz, 2H), 4.59–4.63 (q, J = 5.4 Hz, 1H), 4.89–4.92 (q, J = 5.4 Hz, 1H), 5.29–5.35 (m, 1H), 5.40 (s, 1H), [5.81 (s, 1H)], 7.16–7.22 (m, 3H), 7.25–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 6.26, 13.0, 21.7, 24.0, 32.4, 39.1, 44.6, 86.8, 97.2, 116.9, 125.9, 126.9, 128.9, 130.4, 134.0, 138.9, 156.3; MS (EI, 70 eV): m/z (%) = 299 [M$^+$] (34), 243 (100), 228 (22), 208 (16), 186 (8), 164 (14), 131 (8), 116 (15), 91 (12), 57 (15), 41 (12). *4-Benzylidene-5-butyl-3-cyclohexyl-5-ethyloxazolidin-2-one* (**3d**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2957, 2931, 2858, 1761, 1665; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.83–0.91 (m, 6H), 1.32–1.38 (m, 8H), 1.57–1.85 (m, 10H), 3.15–3.19 (t, J = 7.8 Hz, 1H), [3.62–3.66 (t, J = 7.4 Hz, 1H)], 5.34 (s, 1H), [6.00 (s, 1H)], 7.12–7.19 (m, 3H), 7.25–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 6.1, 13.0, 21.5, 23.9, 25.2, 27.6, 31.2, 37.7, 52.9, 86.4, 98.3, 126.1, 127.1, 128.5, 134.3, 139.7, 154.8; MS (EI, 70 eV): m/z (%) = 341 [M$^+$] (38), 285 (64), 260 (90), 230 (50), 203 (100), 168 (28), 124 (34), 91 (42), 57 (15), 55 (52), 41 (24), 28 (39). *4-Benzylidene-5-butyl-5-ethyl-3-hexyloxazolidin-2-one* (**3e**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2958, 2931, 2861, 1767, 1671; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.72–0.76 (m, 3H), 0.82–0.89 (m, 6H), 1.30–1.36 (m, 10H), 1.63–1.65 (m, 6H), 3.24–3.29 (t, J = 7.2 Hz, 2H), [3.50–3.54 (t, J = 7.8 Hz, 2H)], 5.32 (s, 1H), [5.94 (s, 1H)], 7.12–7.17 (m, 3H), 7.23–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 7.1, 13.9, 22.5, 24.9, 26.1, 26.5, 31.5, 31.9, 33.3,41.3, 88.4, 99.0, 127.0, 128.1, 129.3, 134.9, 140.5, 156.3; MS (EI, 70 eV): m/z (%) = 343 [M$^+$] (34), 287 (100), 252 (25), 230 (35), 202 (34), 188 (22), 131 (15), 117 (26), 91 (44), 55 (18), 43 (32), 28 (38). *4-Benzylidene-3-butyl-5,5-pentamethyleneoxazolidin -2-one* (**3f**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2964, 2935, 2866, 1761, 1686: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.56–0.60 (m, 3H), 0.93–0.97 (m, 2H), 1.58–1.63 (m, 10H), 1.69–1.77 (m, 2H), 3.25–3.28 (m, 2H), [3.49–3.53 (t, J = 7.4 Hz, 2H)], 5.45 (s, 1H), [5.71 (s, 1H)], 7.13–7.19 (m, 3H), 7.21–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.4, 19.2, 21.8, 24.7, 28.9, 37.3, 42.6, 83.9, 98.0, 126.7, 127.8, 129.6, 134.9, 143.2, 156.8; MS (EI, 70 eV): m/z (%) = 299 [M$^+$] (100), 257 (22), 244 (54), 200 (16), 172 (26), 129 (10), 117 (15), 91 (22), 81 (14), 41 (6). *3-Butyl-4-ethylidene-5,5-pentamethyleneoxazolidin-2-one* (**3g**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2961, 2934, 2864, 1764, 1671; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88–0.92 (t, J = 7.4 Hz, 3H), 1.26–1.30 (t, J = 7.8 Hz, 3H), 1.48–1.50 (d, J = 7.6 Hz, 2H),1.62–1.90 (m, 12H), 3.33–3.37 (t, J = 7.4 Hz, 2H), [3.59–3.63 (t, J = 7.6 Hz, 2H)], 4.17–3.23 (t, J = 7.6 Hz, 1H), [4.41–4.46 (t, J = 7.4 Hz, 1H)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 11.5, 13.7, 19.7, 21.5, 24.7, 28.3, 34.1, 40.7, 83.5, 91.7, 141.6, 155.7; MS (EI, 70 eV): m/z (%) = 237 [M$^+$] (55), 208 (24), 195 (44), 182 (100), 164(22), 150 (28), 138 (32), 122 (32), 108 (18), 93 (14), 81 (16), 55 (14), 41 (12), 28(8). *4-Benzylidene-3-butyloxazolidin-2-one* (**3h**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2959, 2934, 2873, 1771, 1661; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.96–1.00 (t, J = 7.4 Hz, 3H), 1.37–1.46 (m, 2H), 1.63–1.71 (m, 2H), 3.36–3.40 (t, J = 7.6 Hz, 2H), [3.56–3.960 (t, J = 7.4 Hz, 1H)], 4.46 (s, 2H), [5.14 (d, J = 2.8 Hz, 2H)], 5.65 (s, 1H), [6.46 (s, 1H)], 7.16–7.20 (m, 3H), 7.25–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 12.8, 19.1, 27.6, 40.6, 66.1, 98.7, 124.8, 126.0, 128.0, 134.5, 134.9, 155.9; MS (EI, 70 eV): m/z (%) = 231 [M$^+$] (100), 201 (24), 174 (32), 161 (18), 130 (20), 118 (38), 91 (72), 78 (20), 41 (12). *4-Benzylidene-3-butyl-5-methyloxazolidin-2-one* (**3i**, *Z/E mixture*): IR (KBr, ν/cm^{-1}): 2960, 2934, 2873, 1770, 1667; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.96–0.99 (t, J = 7.4 Hz, 3H), 1.37–1.45 (m, 2H), 1.62–1.69 (m, 5H), 3.49–3.62 (m, 2H), 5.60 (d, J = 2.8 Hz, 1H), 5.64–5.69 (m, 1H), 7.14–7.19 (m, 3H), 7.25–7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 12.8, 17.9, 19.1, 27.6, 40.3, 73.5, 98.3, 125.2, 126.8, 127.8, 134.2, 140.0, 155.3; MS (EI, 70 eV): m/z (%) = 245 [M$^+$] (100), 190 (40), 145 (32), 130 (34), 117(60), 91 (75), 28 (20).
9. Yamada, W.; Sugawara, Y.; Cheng, H. M.; Ikeno, T.; Yamada, T. *Eur. J. Org. Chem.* **2007**, 2604.