Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 22 (2011) 1063–1066
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Efficient catalyst-free chemical fixation of carbon dioxide into 2-oxazolidinones under supercritical condition

Jing Xiu Xu *, Jin Wu Zhao, Zhen Bin Jia

School of Pharmacy, Guangdong Medical College, Dongguan 523808, China

Received 20 December 2010
Available online 25 June 2011

Abstract

4-Methylene-1,3-oxazolidin-2-ones can be synthesized from propargylic alcohols, primary amines and carbon dioxide under supercritical condition in the absence of any additional catalyst and solvent. Various propargylic alcohols and primary amines were examined.

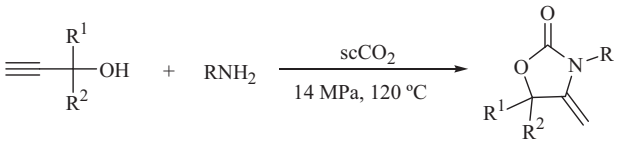
Keywords: Catalyst-free; Carbon dioxide; Supercritical; 2-Oxazolidinone

Oxazolidinones are useful heterocyclic compounds in organic synthesis. They can be used as chiral synthons or chiral auxiliaries in asymmetric syntheses, and they usually exist as necessary moiety in pharmaceutical chemistry owing to their good antibacterial properties [1]. Thanks to the exocyclic double bond, 4-methylene-1,3-oxazolidin- 2-ones can be further transformed [2]. In our previous work, 4-methylene-1,3-oxazolidin-2-ones were prepared *via* the cycloadditon of propargylic alcohols with amines and carbon dioxide (CO_2) catalyzed by transition metal salt cuprous iodide [3]. It was reported that the reaction of propargylic alcohols, primary amines and CO_2 to construct the oxazolidinones could be catalyzed by tri-*n*-butylphosphine which is expensive and toxic [4]. Deng's group disclosed that the three-component reaction could proceed under the catalysis of the costly ionic liquid with cuprous chloride as co-catalyst [5], or without [6]. These approaches to 4-methylene-1,3-oxazolidin-2-ones all suffer the drawback of needing expensive, toxic or metal catalysts.

CO_2 is the most important greenhouse gas produced by human activities, primarily through the combustion of fossil fuels. On the other hand, CO_2 is an abundant, cheap, and nontoxic biorenewable C1 building block in organic synthesis. Therefore, from the viewpoint of green chemistry and carbon reduction, chemical fixation of CO_2 into useful organic compounds has been an essential issue in synthetic organic chemistry during the last two decades [7]. In addition, supercritical carbon dioxide ($scCO_2$, Tc = 31.1 °C, Pc = 7.39 MPa) has been emerged as an environmentally benign alternative to organic solvents because of its advantages in terms of nonflammability, easy separation from reaction mixtures, as well as eco-compatibility, low cost, and availability. Hence, it is quite significant that CO_2 could be used both as an attractive raw material and as a green reaction medium [8]. Herein, we wish to report an efficient and

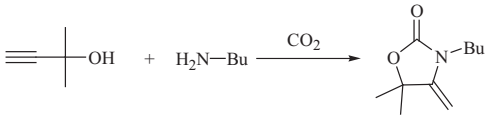
* Corresponding author.
E-mail address: jingxiuxu@sohu.com (J.X. Xu).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2011.04.004



Scheme 1. Catalyst-free chemical fixation of carbon dioxide into 2-oxazolidinones under supercritical condition.

Table 1
Optimizing the reaction conditions for the chemical fixation of CO_2 into 4-methyleneoxazolidin-2-ones with propargylic alcohols and primary amines.[a]



.

Entry	Pressure (MPa)	Temperature (°C)	Time (h)	Yield (%)[b]
1	5	120	10	Trace
2	5	120	24	20
3	5	120	48	49
4	8	120	48	72
5	11	120	48	76
6	14	120	48	84
7	17	120	48	73
8	14	140	48	84
9	14	100	48	70

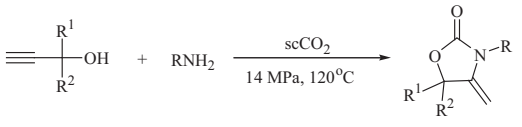
[a] Reagents and conditions: 2-methylbut-3-yn-2-ol (2 mmol), *n*-butylamine (4 mmol).
[b] Determined by GC analysis.

eco-friendly process for conversion of CO_2 into 4-methyleneoxazolidin-2-ones in the absence of any additional catalyst and solvent (Scheme 1).

We first optimized the the reaction conditions for the chemical fixation of CO_2 with 2-methylbut-3-yn-2-ol and *n*-butylamine as model substrates, and the results are summarized in Table 1. When the cycloaddition reaction proceeded at 120 °C under 5 MPa for 10 h [6], only trace amounts of the desired 3-butyl-5,5-dimethyl-4- methyleneoxazolidin-2-one **a** was detected (entry 1). When the reaction time was lengthened from 10 h to 48 h the yields rose from trace to 49% (entries 2, 3). When CO_2 pressure was increased from 5 MPa to 8 MPa, the yield soared from 50% to 72% (entries 3, 4). Presumedly, CO_2 under this pressure became $scCO_2$, playing the role of the reaction medium to improve the three-component assembly. When CO_2 pressure was further raised to 11 MPa and 14 MPa, the yield of the cycloaddition reaction was bettered to 76% and 84%, respectively (entries 5, 6). However, when the pressure was elevated to 17 MPa, the yield of the corresponding 2-oxazolidinone decreased to 73% (entry 7). It was also found that the further raise of the reaction temperature could not promote the yield (entry 8), while the decline of the temperature resulted in an inferior yield (entry 9). Therefore, the best reaction conditions were the factors depicted in entry 6.

We next probed the generality and the limitation of the chemical fixation of CO_2. The results are tabulated in Table 2 [9]. Under the optimal conditions, 2-methylbut-3-yn-2-ol and a variety of primary amines went across the cycloaddition reaction in $scCO_2$, As seen in Table 2, along with *n*-butylamine, allylamine and cyclohexylamine undergo three-component assembly smoothly to afford the desired products **b** and **c** in respectively in 72% and 87% yields, respectively (entries 2, 3). Unfortunately but expectedly, aniline could not undergo the cycloaddition owing to its poor nucleophilicity (entry 4). Our study suggested that the steric hindrance of the substituents on the primary amines had strong impact on the chemical fixation of CO_2. *sec*-Butylamine carrying a bulkier substituent gave lower yield than *n*-butylamine (entry 5), and *tert*-butylamine could not produce the desired product at all (entry 6). *n*-Butylamine was then treated with various propargylic alcohols. 2-Phenylbut-3-yn-2-ol furnished the expected product **g** in excellent 88% yield (entry 7), and the product **h** was obtained in 84% yield from 1-ethynylcyclohexanol (entry 8),

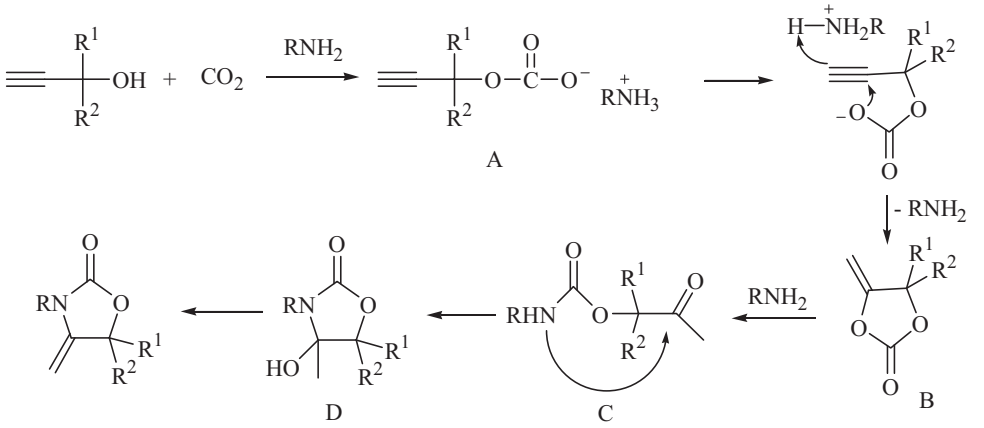
Table 2
Chemical fixation of CO_2 into 4-methyleneoxazolidin-2-ones with the corresponding propargylic alcohols and primary amines under supercritical condition.[a]



.

Entry	R^1	R^2	R	Yield (%)[b]
1	Me	Me	*n*-Bu	80 (**a**)
2	Me	Me	Allyl	72 (**b**)
3	Me	Me	Cy	87 (**c**)
4	Me	Me	Ph	0[c] (**d**)
5	Me	Me	*sec*-Bu	70 (**e**)
6	Me	Me	*t*-Bu	0[d] (**f**)
7	Ph	Me	*n*-Bu	88 (**g**)
8	$-C_5H_{10}-$		*n*-Bu	84 (**h**)
9	*i*-Pr	Me	*n*-Bu	70 (**i**)
10	*n*-C_6H_{13}	Me	*n*-Bu	65 (**j**)

[a] Reagents and conditions: alcohol (2 mmol), amine (4 mmol), Pco_2 = 14 MPa, 120 °C.
[b] Isolated yield.
[c] No desired product detected.
[d] 2-Methylbut-3-yn-2-ol remained unchanged.



Scheme 2. Proposed mechanism for the catalyst-free chemical fixation of carbon dioxide into 2-oxazolidinone.

3,4-dimethylpent-1-yn-3-ol and 3-methylnon-1-yn-3-ol afforded the corresponding products **i** and **j** in yields of 70% and 65%, respectively (entries 9, 10).

Based on the above experimental results, a proposal mechanism is illustrated in Scheme 2. Ammonium carbonate **A** is firstly formed by the reaction of propargylic alcohol, amine and CO_2, which may undergoes cyclization with the help of a proton to furnish the α-methylene cyclic carbonate **B** [10]; then amine attacks the carbonyl group of the α-methylene cyclic carbonate to generate the 2-oxoalkyl carbamate **C**. Its nitrogen atom launches intramolecular attack on the carbonyl to give 4-hydroxy cyclic carbamate **D** whose 4-hydroxy is eliminated with the hydrogen atom of 4-methyl to afford the corresponding 4-methylene-2-oxazolidinone [3].

In conclusion, we have developed an efficient and eco-friendly process to fix CO_2 into 4-methyleneoxazolidin- 2-ones with propargylic alcohols and primary amines under supercritical condition, dispensing with any additional catalyst and solvent. In this method, carbon dioxide was employed not only as reaction medium, but also as starting material.

Acknowledgments

This work was supported financially by Youth Foundation of Guangdong Medical College (No. XQ1029) and Science and Technology Planning Project of Zhanjiang city (No. 2009c3103024).

References

[1] M.E. Dyen, D. Swern, Chem. Rev. 67 (1967) 197.
[2] O. Merino, B.M. Santoyo, L.E. Montiel, et al. Tetrahedron Lett. 51 (2010) 3738.
[3] H.F. Jiang, J.W. Zhao, A.Z. Wang, Synthesis (2008) 763.
[4] J. Fournier, C. Bruneau, P.H. Dixneuf, Tetrahedron Lett. 31 (1990) 1721.
[5] Y.L. Gu, Q.H. Zhang, Z.Y. Duan, et al. J. Org. Chem. 70 (2005) 7376.
[6] Q.H. Zhang, F. Shi, Y.L. Gu, et al. Tetrahedron Lett. 46 (2005) 5907.
[7] T. Sakakura, J.C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
[8] P. Licence, J. Ke, M. Sokolov, et al. Green Chem. 5 (2003) 99.
[9] Spectral data for selected products: compound **c** (Table 2 entry 3): IR (KBr, ν/cm^{-1}): 2932, 2854, 1736, 1680; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.19 (d, 1H, J = 2.8 Hz), 3.91 (d, 1H, J = 2.8 Hz), 3.50 (m, 1H), 2.04–2.08 (m, 2H), 1.81 (d, 2H, J = 10.4 Hz), 1.63 (d, 3H, J = 9.4 Hz), 1.43 (s, 6H), 1.26–1.36 (m, 2H), 1.10–1.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 150.6, 81.3, 80.1, 53.9, 33.2, 28.6, 28.2, 25.5; MS (EI, 70 eV): m/z = 209 (M^+), 128, 112, 84, 55, 41; compound **g** (Table 2 entry 7): IR (KBr, ν/cm^{-1}): 2939, 2870, 1758; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.44 (m, 5H), 4.20 (d, 1H, J = 3.2 Hz), 4.09 (d, 1H, J = 2.8 Hz), 3.40 − 3.52 (m, 2H), 1.83 (s, 3H), 1.55–1.62 (m, 2H), 1.30–1.35 (m, 2H), 0.88–0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 149.5, 141.1, 128.7, 127.9, 125.0, 91.5, 82.3, 28.4, 27.3, 20.4 13.9; MS (EI, 70 eV): m/z = 245 (M^+), 190, 158, 144, 129, 97, 77, 41.
[10] C.R. Qi, H.F. Jiang, Green Chem. (2007) 1284.