Silver-catalyzed Preparation of Oxazolidinones from Carbon Dioxide and Propargylic Amines

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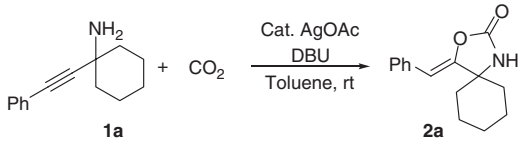
The silver-catalyzed carbon dioxide incorporation reaction into various propargylic amines proceeded under mild reaction conditions to obtain the corresponding oxazolidinone derivatives in high to excellent yields. The geometry of the C–C double bond in product was confirmed to be the Z isomer by X-ray analysis.

Carbon dioxide has drawn much attention from the viewpoint of global warming as well as one of the most promising alternatives to phosgene.[1] The oxazolidinone preparation from carbon dioxide is also a most attractive synthetic method. Much effort has been made to develop the chemical fixation of carbon dioxide into propargylic amines to provide the oxazolidinone derivatives. For example, it was reported that transition-metal salts, such as copper,[2a,2b] ruthenium,[2c] and palladium,[2d,2e] were employed as efficient catalysts to promote the reaction of propargylic amine and carbon dioxide, however, the applicable substrates in these catalyses were limited to terminal alkynes[2a–2e] or N-substituted propargylic amines.[2a–2d] The super bases, such as MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene),[3a] guanidine derivatives,[3b] and DBU,[3c] and an electrochemical method[4] were initially attempted to accelerate this reaction, though the N-substituted propargylic amines[3a–3c,4] were required to achieve high yields of the corresponding oxazolidinone derivatives, or the terminal alkynes[4] were only applicable with a decreased reactivity to afford the product in low yield.[3a,3b] Recently, supercritical conditions were applied to the incorporation of carbon dioxide into propargylic amines in the presence of basic alumina[5a] or without any additives.[5b] Even under these conditions, the substrates to afford the oxazolidinones in high yield were still limited to the N-substituted terminal alkynes[5a] or aryl-substituted internal alkynes.[5b] In spite of various reports on the incorporation of carbon dioxide into propargylic amines, practical procedures for the reaction of propargylic amines with internal alkynes or N-unsubstituted amines have never been achieved. Also, it should be pointed out that almost all the reported methods require severe reaction conditions, such as high temperature and/or high carbon dioxide pressure. In a previous communication,[6] the combined use of a catalytic amount of a silver salt with DBU was reported to efficiently catalyze CO_2 incorporation under mild reaction conditions into a wide range of propargylic alcohols to afford the corresponding cyclic carbonates in high to excellent yields. It was found that this procedure could be successfully applied to various terminal and internal N-substituted and N-unsubstituted propargylic amines to afford the corresponding 1,3-oxazolidin-2-ones in high to excellent yield under mild reaction conditions. In this communication, we report the efficient preparation of oxazolidinones from carbon dioxide and propargylic amines catalyzed by silver salts.

1-(Phenylethynyl)cyclohexanamine (**1a**), a model compound of an N-unsubstituted propargylic amine with an internal alkyne, was first subjected to standard conditions; In the presence of 10 mol % silver acetate and a stoichiometric amount of DBU in toluene under 1.0 MPa CO_2 pressure at room temperature, the corresponding oxazolidinone **2a** was obtained in 95% yield after 2 h (Table 1, Entry 1). The reaction proceeded so smoothly that milder reaction conditions were examined involving the CO_2 pressure, the amount of silver catalyst and DBU in the reaction of **1a** at room temperature (Table 1). Under atmospheric pressure of CO_2, the corresponding product was obtained in an excellent yield (Entry 2). It was found that in the absence of DBU, the product was obtained in 87% yield (Entry 3). The mechanism for the present reaction was assumed to be that the carbamate intermediate derived from propargylic amine with carbon dioxide successively reacted with the alkyne activated by the silver catalyst to afford the oxazolidinone via an intramolecular ring-closing reaction. Although DBU base would assist with the carbamate formation, in equilibrium between the corresponding ammonium carbamate and free propargylic amine under a CO_2 atmosphere,[5b] the amine could work as a base to assist with the carbamate formation without DBU. In the reaction with 2 mol % silver acetate under a 0.3 MPa CO_2 pressure, the propargylic amine **1a** was completely consumed to afford the product in excellent yield (Entry 4). Various solvents were screened expecting the effective solvation of carbamate intermediate to accelerate the reaction.[7] When DMSO was employed as solvent, the reaction was accelerated dramatically to afford the product in 98% yield after 10 h even under atmospheric pressure CO_2 (Entry 5).

Table 1. Examination of various reaction conditions



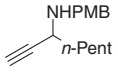
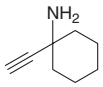
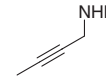
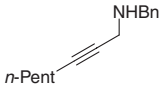
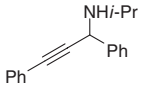
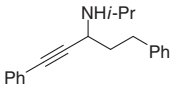
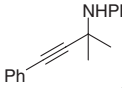
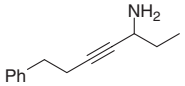
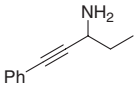
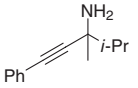
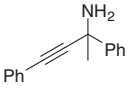
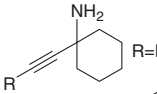
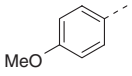
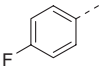
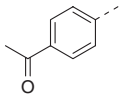
1a **2a**

Entry[a]	CO_2 pressure /MPa	AgOAc /mol %	DBU /mol %	Time/h	Yield/%[b]
1	1.0	10	100	2	95
2	0.1	10	100	6	95
3	1.0	10	0	46	87
4[c]	0.3	2	0	47	91
5[c,d]	0.1	2	0	10	98

[a]The reaction was carried out in 1.0 mL of toluene with 0.25 mmol of substrate at room temperature. The reaction proceeded under homogeneous conditions. [b]Isolated yield. [c]The reaction was carried out in 1.5 mL of toluene with 0.50 mmol of substrate. [d]The reaction was carried out in DMSO at 25 °C.

The optimized catalytic system was successfully applied to various propargylic amines (Table 2). Propargylic amines with terminal alkyne and N-substituted amines were converted into

Table 2. Various propargylic amines

Entry[a]	Propargylic amine		Time/h	Yield/%[b]
1		**1b**	7.0	95
2		**1c**	7.0	97
3		**1d**	4.0	95
4		**1e**	3.0	99
5		**1f**	1.5	95
6		**1g**	2.0	99
7		**1h**	1.5	99
8		**1i**	3.0	97
9		**1j**	7.0	77
10		**1k**	5.0	97
11		**1l**	3.0	99
12		**1m**	4.0	quant.
13		**1a**	10	98
14		**1n**	2.5	94
15		**1o**	3.0	99
16		**1p**	7.0	94
17		**1q**	3.0	97
18		**1r**	7.0	89

[a]Reaction conditions: The reaction was carried out in 1.5 mL of DMSO with 2 mol % silver acetate and 0.50 mmol of substrate under 0.1 MPa CO_2 pressure at 25 °C. [b]Isolated yield.

the corresponding oxazolidinones **2b** and **2c** in excellent yield (Entries 1 and 2). Also the reaction of N-unsubstituted propargylic amines with the terminal alkyne **1d** proceeded in high yield (Entry 3). The N-substituted internal alkynes, alkyl-substituted alkyne **1e** and **1f** and aryl-substituted alkyne **1g**–**1i**, reacted with CO_2 to afford the corresponding oxazolidinone in high yield (Entries 4–8). It should be pointed out here that in the present catalytic system, the N-unsubstituted propargylic amines with an internal alkyne, which have never been reported in a CO_2 incorporation reaction, were smoothly converted into the corresponding cyclic products under mild conditions. The alkyl-substituted (**1j**, Entry 9), aryl-substituted (**1a** and **1k**–**1p**, Entries 10–16), and heteroaryl-substituted (**1q** and **1r**, Entries 17 and 18) alkynes were converted into the corresponding oxazolidinones in high yield. As for the exo olefin structure, all products were obtained as a sole isomer based on an NMR spectroscopic analysis, and they were suggested to be the Z isomer by NOE experiments. The geometry of the C–C double bond in product **2a** was confirmed to be the Z isomer by X-ray analysis.[7]

It is noted that the CO_2 incorporation reaction into various propargylic amines proceeded using a catalytic amount of silver acetate under mild reaction conditions to obtain the corresponding oxazolidinone derivatives in high yields. Further investigations on application of the present catalytic system for stereoselective syntheses are now under way.

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