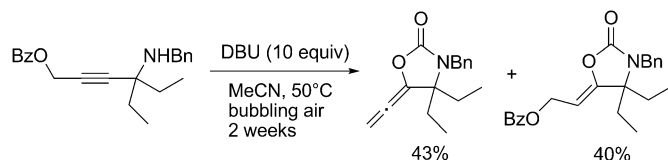


Synthesis of Oxazolidinones by Efficient Fixation of Atmospheric CO₂ with Propargylic Amines by using a Silver/1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) Dual-Catalyst System

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Chemical fixation of CO₂ has received much attention because of the potential use of CO₂ as an abundant carbon source and the variety of organic molecules that can be synthesized by the fixation of CO₂.^[1] Most of these transformations require an excess of CO₂ and, therefore, large amounts of CO₂ are used annually for chemical synthesis on an industrial scale. On the other hand, the concentration of CO₂ in the atmosphere has been increasing steadily, which is considered to have an impact on the global climate.^[2] The fixation of atmospheric CO₂ thus represents an attractive area of study in both organic and green chemistry. Various inorganic and organic compounds, such as metal complexes,^[3] N-heterocyclic carbenes,^[4] ureas,^[5] and diamines,^[6] have been utilized for the purpose of capturing atmospheric CO₂. We have recently reported a synthesis of oxazolidinone by the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-promoted reaction of a propargylic amine by bubbling air through the reaction mixture (Scheme 1).^[7,8] This result is the first example of the



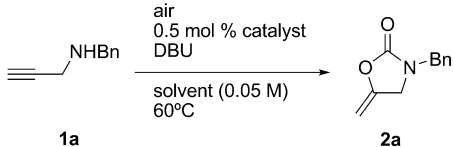
Scheme 1. DBU-promoted fixation of atmospheric CO₂. Bn = benzyl, Bz = benzoyl.

fixation of atmospheric CO₂ into an organic molecule with the concomitant formation of a covalent bond. However, the reaction is an isolated example. Furthermore, a long reaction time (2 weeks) and an excessive amount of DBU (10 equiv) were required to complete the reaction on account of the low concentration of CO₂ in air (0.04% v/v). To increase the utility of this reaction, we investigated various

reaction conditions. Herein, we report a practical methodology for the fixation of atmospheric CO₂, in which substituted oxazolidinones have been efficiently synthesized by conducting the reaction using a silver/DBU dual-catalyst system.

The reactions were initially attempted by using *N*-benzylpropargylamine (**1a**) (Table 1). Substrate **1a** was treated with PtCl₂ (0.5 mol %) and DBU (200 mol %) in DMSO/

Table 1. Optimization of the reaction conditions.



Entry	Catalyst	Solvent	DBU [mol %]	Time [h]	Yield [%]
1	PtCl ₂	DMSO/H ₂ O ^[a]	200	240	69
2	CuI	DMSO/H ₂ O ^[a]	200	120	63
3	Cu(OAc) ₂	DMSO/H ₂ O ^[a]	200	114	78
4	AgOAc	DMSO/H ₂ O ^[a]	200	24	86
5	AgOAc	DMSO	200	18	90
6	Ag ₂ O	DMSO	200	16	92
7	AgNO ₃	DMSO	200	17	95
8	AgNO ₃	DMSO	10	33	94
9	AgNO ₃	DMSO	0	–	N.R.
10	none	DMSO	10	48	8
11 ^[b]	AgNO ₃	DMSO	10	27	95
12 ^[c]	AgNO ₃	DMSO	10	20	95

[a] 10:1 ratio of DMSO/H₂O was used as the solvent. [b] Reaction in 0.1 M solution. [c] Reaction in 0.2 M solution. N.R. = no reaction.

H₂O (10:1) and the stirring was continued vigorously under air at 60°C for 240 h (Table 1, entry 1). The reaction successfully ran to completion, affording the desired oxazolidinone, **2a**, in 69% yield. Further optimization reactions in which various transition-metal catalysts (Table 1, entries 2–4) were applied revealed that the reaction was complete in 24 h, giving **2a** in 86% yield in the presence of AgOAc^[8] (Table 1, entry 4). A better result was obtained when the reaction was conducted in DMSO (Table 1, entry 5), and the yield was increased to 95% when AgNO₃ was used as the catalyst (Table 1, entry 7). Similar reactivity was observed even in the presence of only 10 mol % DBU (Table 1, entry 8). On the other hand, no reaction occurred in the absence of DBU (Table 1, entry 9). Similarly, the yield of **2a**

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201203366>.

was dramatically decreased to 8% when AgNO₃ was not added (Table 1, entry 10). These results indicate that, among the candidates tested, both a silver complex and DBU are necessary to promote the efficient fixation of atmospheric CO₂. The reaction rate was enhanced by increasing the concentration of the reactants in the solvent (Table 1, entries 11 and 12) and the best result was obtained when the reaction was carried out in a 0.2 M solution (Table 1, entry 12).

Having identified a useful set of reaction conditions, we subsequently examined reactions by using various propargylic amines **1b–1m** (Table 2). The reaction of *N*-(4-methoxybenzyl)propargylamine (**1b**) successfully proceeded to afford the oxazolidinone **2b** in 89% yield (Table 2, entry 1). The propargylic amines **1c–1f**, having a substituent at the propargylic position, also reacted with atmospheric CO₂ to

produce the corresponding products **2c–2f** in good yields (Table 2, entries 2–5). When the reaction of substrate **1g**, containing a hydroxyethyl group, was conducted, the desired oxazolidinone **2g** was obtained in 33% yield together with tetrahydrooxazinone **3g** in 30% yield (Table 2, entry 6). The reaction of the TMS-substituted propargylic amine **1h** afforded the desilylated oxazolidinone **2a** in 92% yield (Table 2, entry 7). Substrates **1i** and **1j**, containing a siloxy- and a hydroxymethyl group at the terminal position, were stereoselectively converted to the oxazolidinones **2i** and **2j** in 86 and 66% yields, respectively (Table 2, entries 8 and 9). When the substrates **1k–1m**, containing a methyl, an ethyl, and a hydroxyethyl group, were subjected to the reaction conditions, the corresponding products **2k–2m** were obtained in moderate yields (Table 2, entries 10–12). In these

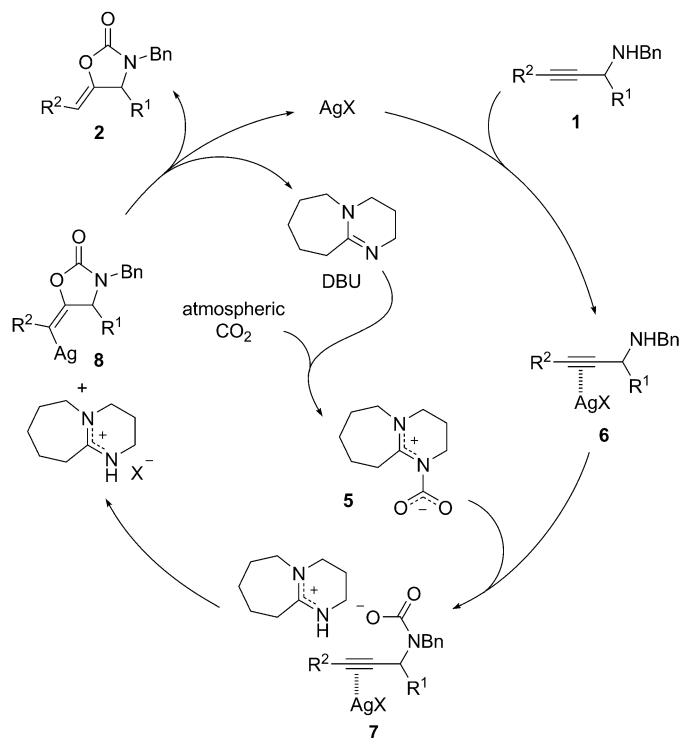
Table 2. Fixation of atmospheric CO₂ by using various propargylic amines **1b–m**.^[a]

Entry	Substrate 1	Products	Yields [%]	Entry	Substrate 1	Products	Yields [%]
1 ^[b]			89	7 ^[b]			92
2 ^[c]			87	8 ^[c]			86
3 ^[b]			89	9 ^[d]			66
4 ^[d]			78	10 ^[d]			73 (2k)
5 ^[d]			87	11 ^[d]			68 (2l)
6 ^[c]			33 (2g)	12 ^[d]			77 (2m)
			30 (3g)				9 (4k)
							14 (4l)
							13 (4m)

[a] The reactions were carried out in the presence of AgNO₃ and DBU in DMSO (0.2 M) at 60 °C. [b] 0.5 mol % AgNO₃ and 200 mol % DBU were used. [c] 0.5 mol % AgNO₃ and 10 mol % DBU were used. [d] 2.0 mol % AgNO₃ and 200 mol % DBU were used.

reactions, the dihydrooxazinones **4k–4m** were also produced as byproducts in low yields.

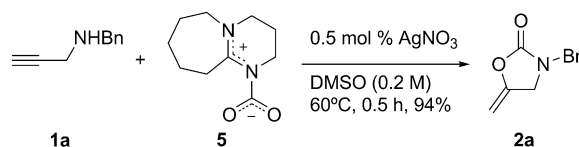
A plausible mechanism, which may account for the efficient fixation of atmospheric CO₂ by this process, is shown in Scheme 2. Atmospheric CO₂ is initially trapped by DBU to form the DBU–CO₂ complex **5** in situ that then reacts



Scheme 2. Proposed reaction mechanism.

with the silver-coordinated propargylic amine **6** to afford the carbamate **7** by transferring CO₂. Then, intramolecular 5-*exo*-cyclization followed by proto-demetalation from the intermediate **8** produces the oxazolidinone **2** with regeneration of the silver complex and DBU. In the case of the substituted substrates **1k–1m**, intramolecular 6-*endo*-cyclization of **7** also proceeds to afford the dihydrooxazinones **4k–4m** as the minor products.^[9] The tetrahydrooxazinone **3g** resulting from the hydroxyethyl-substituted substrate **1g**, could result from an intramolecular transcarbamation of the oxazolidinone **2g**.

It is known that DBU reacts with CO₂ to form DBU–CO₂ complex **5**, which acts as the CO₂ source for various CO₂-fixation reactions.^[10] To examine the effect of DBU on the synthesis of vinylideneoxazolidinone, the reaction of the propargylic amine **1a** with DBU–CO₂ complex **5** was attempted. When **1a** was treated with **5** in the presence of AgNO₃ in DMSO at 60°C, the reaction was completed in 30 min to produce the corresponding oxazolidinone **2a** in 94% yield (Scheme 3). This result implies that the CO₂-fixation process proceeds through the formation of DBU–CO₂ complex **5**.



Scheme 3. Attempted reaction of propargylic amine **1a** with DBU–CO₂ complex **5**.

In conclusion, we have developed a methodology for the synthesis of oxazolidinones by the fixation of atmospheric CO₂ with propargylic amines. Efficient fixation of CO₂ has been achieved by the use of a silver/DBU dual-catalyst system. The reaction afforded a variety of substituted oxazolidinones in good yields, and the process provided a new and practical protocol for the utilization of air as a source of CO₂. Further studies regarding this type of reaction and the synthetic application of the resulting oxazolidinones are now in progress.

Acknowledgements

This research was conducted as part of the Adaptable & Seamless Technology Transfer through Target-driven R&D (A-STEP) Program of the Japan Science and Technology Agency (JST), and the Program for the Promotion of Basic and Applied Research for Innovations in the Bio-oriented Industry (BRAIN).

Keywords: amines • carbon dioxide fixation • organic bases • oxazolidinones • propargylic amines • silver

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Received: September 20, 2012
Published online: November 7, 2012