

# Silver-Catalyzed Efficient Synthesis of Vinylene Carbonate Derivatives from Carbon Dioxide

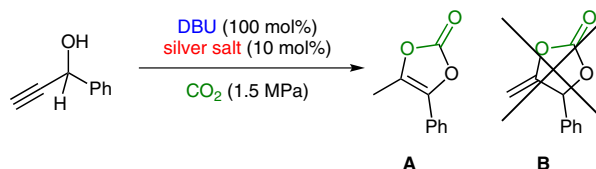
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**Abstract:** It was found that the silver salt and base was an efficient catalytic system for the reaction of the secondary propargylic alcohol with carbon dioxide to afford various corresponding vinylene carbonate derivatives in good to high yields under mild conditions.

**Key words:** alkynes, vinylene carbonates, carbon dioxide, silver, isomerization, Lewis acids



**Scheme 1** Formation of vinylene carbonate

Carbon dioxide is usually generated as a waste in the human living process. Much effort has been expended for the development of the effective utilization of carbon dioxide in organic syntheses. However, carbon dioxide is thermodynamically stable and has a low reactivity due to the highly oxidized state of the carbon atom. Therefore, high temperature and high pressure are required to obtain satisfactory results.

We recently reported that a silver catalyst could efficiently mediate the carbon dioxide incorporation into various alkynyl derivatives to afford the corresponding cyclic carbonate, oxazolidinone, lactone, and benzoxazin-2-one derivatives with the *Z*-olefin under mild reaction conditions.<sup>1</sup> In these reactions, the efficient activation of the C–C triple bond by silver salts would be the key step for producing the corresponding products in high yields, which was supported by DFT calculations of the model substrate with a model base.<sup>2</sup> It was reported that the reaction of tertiary propargylic alcohols and carbon dioxide was catalyzed by silver acetate with DBU to afford the corresponding cyclic carbonate in high to excellent yields.<sup>1a</sup> When we applied this catalytic system to the reaction of a secondary propargylic alcohol, the predicted cyclic carbonate was not obtained although another new spot was detected by TLC analysis. After some additional analyses of this compound including NMR, FTIR, and GC–MS, it was found that the vinylene carbonate derivative **A** was produced (Scheme 1).

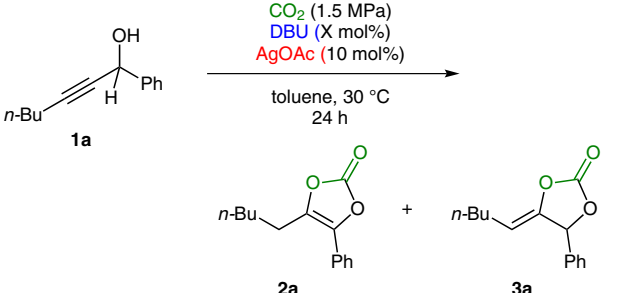
Vinylene carbonate derivatives are useful as the prodrug for drug-delivery systems<sup>3</sup> and are used as an electrolyte additive of lithium ion batteries,<sup>4,5</sup> however, there are few synthetic methods of the vinylene carbonate derivatives. It was reported that the vinylene carbonate derivative was produced by the reaction of an  $\alpha$ -hydroxy ketone and its synthetic equivalent with phosgene,<sup>6</sup> but phosgene is

known to be a highly toxic reagent, thus a safer method was required. Although some improved methods in which bis(trichloromethyl)carbonate<sup>7</sup> or carbodiimidazole<sup>8</sup> was used as the alternative reagent of phosgene were developed, the number of substrates was still limited. The dehydrogenchlorination from chloroethylene carbonate was also reported to afford the corresponding vinylene carbonate derivatives.<sup>9</sup> However, in order to obtain the starting material, it required the radical chlorination of cyclic carbonate with chlorine and ultraviolet light. It was also reported that the aryl-substituted vinylene carbonate was formed by the coupling reaction of vinylene carbonate with aryl bromide,<sup>10</sup> however, much waste was generated as a salt. Therefore, the reaction illustrated in Scheme 1 would be an attractive and ideal method for the synthesis of vinylene carbonate derivatives without any waste and using the much safer carbon dioxide instead of phosgene. We now report the efficient synthesis of aryl-substituted vinylene carbonate catalyzed by a silver salt from carbon dioxide.

The reaction of propargylic alcohol **1a** with carbon dioxide was carried out with silver acetate and one equivalent of DBU under the same previously reported conditions. However, the yield was not satisfactory (58% yield) and the starting alcohol **1a** remained with the low material balance. Although an excess of DBU was employed for this reaction in order to improve the yield, the yield had decreased to 29% contrary to our expectation. These results initially urged us to investigate the quantity of DBU (Table 1). When the amount of DBU was gradually decreased from 100 mol% to 40 mol%, the yield was increased and it was found that the corresponding product **2a** was obtained in 94% yield in the presence of 40 mol% DBU (Table 1, entries 2–6).<sup>11–13</sup> However, the yield of the corresponding vinylene carbonate **2a** had decreased to 70% when 30 mol% DBU was used, and the corresponding cyclic carbonate **3a** was formed in 18% yield (Table 1, entry 7). The yield of **2a** drastically decreased in the presence of 20 mol% DBU although the cyclic carbonate

**3a** was obtained in 23% yield (Table 1, entry 8). No products (**2a** and **3a**) were observed when the amount of DBU decreased to 10 mol% (Table 1, entry 9).

**Table 1** Examination of DBU Quantity<sup>a</sup>



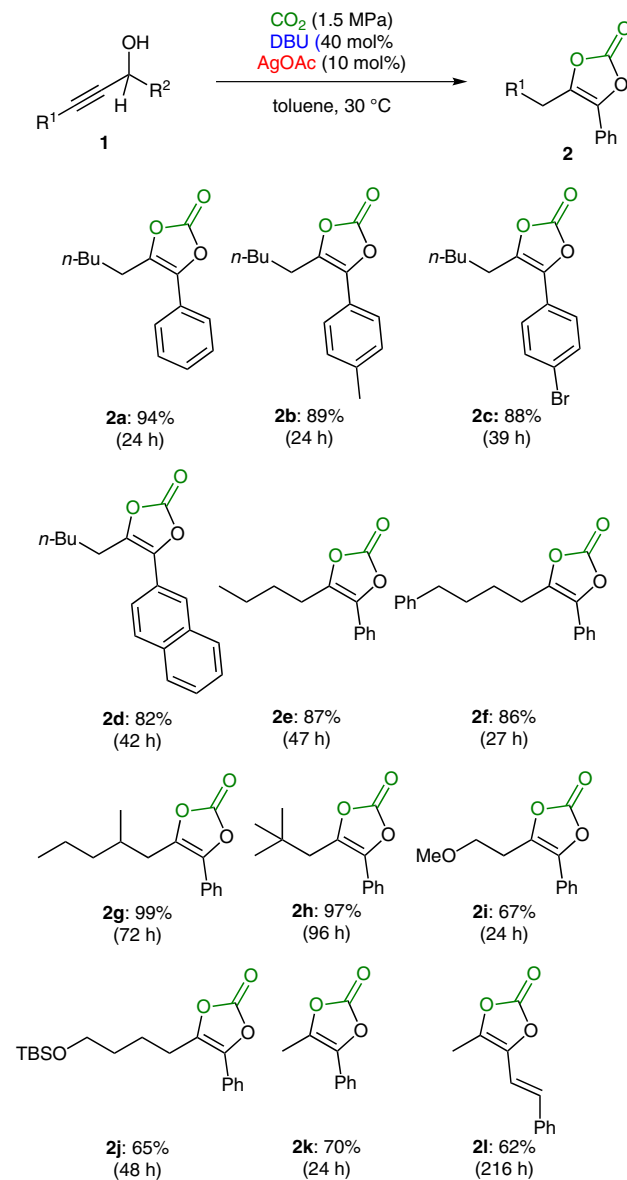
Entry	DBU (mol%)	Yield of <b>2a</b> (%) <sup>b</sup>	Yield of <b>3a</b> (%) <sup>b</sup>
1	150	29	—
2	100	58	—
3	80	60	—
4	60	83	—
5	50	86	—
6	40	94	—
7	30	70	18
8	20	39	23
9	10	trace	trace

<sup>a</sup> The reaction was performed on a 0.3 mmol scale.

<sup>b</sup> Isolated yields.

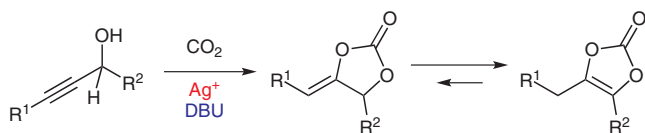
The reactions of several secondary alcohols with carbon dioxide were carried out in the presence of 10 mol% silver acetate with 40 mol% DBU (Scheme 2). The substrates derived from hex-1-yne were initially subjected to these reaction conditions. The reaction of secondary propargylic alcohols having a 4-tolyl group (**1b**), 4-bromophenyl group (**1c**), and 2-naphthyl group (**1d**) were smoothly performed using this reaction system to afford the corresponding vinylene carbonate derivatives **2a–d** in high yields. Next, the reactions of various alkyl-substituted alkyne derivatives were carried out. The substrates **1e** and **1f** having a linear aliphatic alkyne, such as pent-1-yne and 5-phenylpent-1-yne, were transformed into the corresponding products **2e** and **2f** in high yields, respectively. This catalytic system was also applied to the reaction of branched aliphatic alkyne derivatives, such as 3-methylhex-1-yne and 3,3-dimethylbut-1-yne derivatives **1g** and **1h**, to produce the corresponding vinylene carbonate derivatives **2g** and **2h** in excellent yields. It was found that the ether group and siloxy group used under the stated reaction conditions and the corresponding vinylene carbonate derivatives **2i** and **2j** were obtained in good yields, respectively. This catalytic system was also employed for

the reaction of 1-phenylprop-2-yn-1-ol (**1k**) to produce the corresponding product **2k** in 70% yield. When silver(II) picolinate was used as the silver salt instead of silver acetate, the reaction of the substrate having the cinnamyl moiety proceeded to afford the corresponding vinylene carbonate **2l** in good yield although a longer reaction time was required.



**Scheme 2** The reaction of secondary propargylic alcohols (see the Supporting Information for reaction conditions). Isolated yield is described. <sup>a</sup> For compound **2l**: silver(II) picolinate was used instead of silver acetate.

A plausible reaction mechanism was assumed to be as follows (Scheme 3): the cyclic carbonate would be first formed and then isomerization of the olefin would occur to afford the more thermodynamic stable vinylene carbonate derivatives.<sup>14</sup>



**Scheme 3** Plausible reaction mechanism of the formation of vinylene carbonate

In summary, it was found that the silver salt/DBU system was applied to the reaction of secondary propargylic alcohols including internal and terminal alkyne derivatives with carbon dioxide and various corresponding vinylene carbonates were produced in good to high yields. Based on this catalytic system, the substrate having the cinnamyl moiety was found to be transformed into the corresponding vinylene carbonate in good yield when silver(II) picolinate was used as the silver salt. Further investigations are currently under way.

**Supporting Information** for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

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- (11) When the reaction was carried out under the balloon pressure, the yield was decreased into 77% yield.
- (12) **General Procedure**  
The reaction was performed using a pressure test tube equipped with a stirring bar in a 50 mL autoclave. To a solution of propargyl alcohol **1** (0.30 mmol) and AgOAc (0.030 mmol, 5.0 mg) in toluene (2.0 mL) was added DBU (0.12 mmol, 18  $\mu$ L) under an inert gas. Immediately, CO<sub>2</sub> gas was purged, and the reaction mixture was stirred at 30 °C under 1.5 MPa CO<sub>2</sub> pressure. After the reaction was completed, the purification by column chromatography [SiO<sub>2</sub>, eluted with *n*-hexane–EtOAc (100:1)] gave the corresponding carbonate **2**.
- (13) **Representative Experimental Data**  
**4-Pentyl-5-phenyl-1,3-dioxol-2-one (2a)**  
Reaction time 24 h; yield 96%; 66.9 mg; colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.91 (t, *J* = 7.1 Hz, 3 H), 1.37 (m, 4 H), 1.71 (m, 2 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 7.37–7.48 (m, 5 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.9, 22.3, 24.8, 26.5, 31.1, 125.2, 125.6, 128.9, 129.0, 137.2, 139.2, 152.4. IR (KBr): 2958, 2932, 2862, 1821, 1449, 1248, 1188, 1098, 1057, 1026, 977, 760, 692. ESI-HRMS: *m/z* calcd for C<sub>14</sub>H<sub>17</sub>O<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup>: 233.1172; found: 233.1177.
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