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Silver-Catalyzed Incorporation of Carbon Dioxide into Propargylic Alcohols

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Dedicated to the late Professor Yoshihiko Ito for his outstanding contribution to synthetic organic chemistry

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The combined use of a catalytic amount of silver acetate and a stoichiometric amount of DBU efficiently catalyzed the incorporation of CO_2 under mild reaction conditions into a wide range of propargylic alcohols bearing a terminal or an internal triple bond to afford the corresponding cyclic carbonates in high-to-excellent yields. All the cyclic carbonates obtained from the reaction were found to be single isomers. The geometries were determined to be (*Z*) by X-ray crystal structure analysis and NOE experiments.

Introduction

Carbon dioxide is regarded as a C_1 chemical feedstock, though few synthetic processes have been developed because of its thermodynamic stability.[1] Recently, we first reported the enantioselective incorporation of carbon dioxide into an epoxide in the presence of a catalytic amount of optically active ketoiminatocobalt complex catalysts. The racemic glycidol derivatives, such as *N*,*N*-diphenylaminomethyloxirane, reacted with gaseous carbon dioxide to afford the corresponding cyclic carbonate along with the optically active starting epoxide.[2] During the course of our continuing study on the incorporation reaction of carbon dioxide into organic compounds, we found that the combined use of the catalytic amount of silver acetate and stoichiometric amount of DBU was an efficient catalyst system for the incorporation reaction of carbon dioxide with various propargylic alcohols to afford the corresponding cyclic carbonates in high-to-excellent chemical yields under mild reaction conditions.

It was reported that a cyclic carbonate was obtained from carbon dioxide with a readily available propargylic alcohol by using metal salts or phosphanes as a catalyst;[3] however, these reported methods required harsh reaction conditions, such as a high CO_2 pressure and high reaction temperature. It should also be pointed out that terminal alkynes were only applicable for these carbonate formations, and the internal alkynes afforded sluggish results. More recently, super critical conditions were employed for the incorporation of CO_2 into propargylic alcohols, including internal alkynes, by using a phosphane catalyst.[4] However, the substrates that were used were still limited to aryl-substituted propargylic alcohols without any bulky group on the propargylic position.

Results and Discussion

The reaction mechanism for the incorporation of carbon dioxide into propargylic alcohols was assumed as follows: The alcohol, activated by the amine base, would react with carbon dioxide to generate a carbonate intermediate. An intramolecular ring-closing reaction would then proceed on the alkyne, which would be activated by the metal complex to afford the corresponding cyclic carbonate with the release of the metal complex catalyst (Scheme 1). The activation of the alkyne by the metal complex catalyst was proposed to be crucial to drive the present reaction. Nucleophilic addition to activated acetylenes catalyzed by metal salts is a promising method that can be used to obtain various alkenes; for example, cyclic carbonates obtained from a propargylic *tert*-butyl carbonate through an intramolecular nucleophilic ring-closing reaction of the carbonate onto the activated alkyne by a gold(I) catalyst was reported.[5] We

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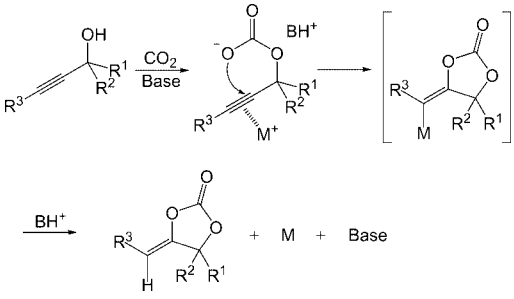
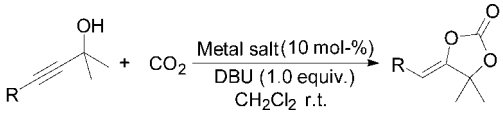
examined various transition metal salts to activate the triple bond with the use of internal alkyne **1b** at room temperature under a carbon dioxide pressure of 2.0 MPa (Table 1). Unfortunately, almost all metals including rhodium,[6] mercury,[7] platinum,[8] and palladium[9] that were expected to activate the acetylenes, were inert in the catalysis of the reaction (Table 1, Entries 1–5). The copper(I) salt produced a trace amount of the cyclic carbonate, and gold was inactive for the present reaction (Table 1, Entries 6 and 7). It was found that by using silver salts as a catalyst in the presence of a stoichiometric amount of DBU, the cyclic carbonate could be quantitatively obtained (Table 1, Entries 8 and 9). The counter ion of the silver salt was then examined in the reaction of propargylic alcohol **1g** possessing an alkyl-substituted internal alkyne. In the presence of 10 mol-% of silver perchlorate, the reaction smoothly proceeded to afford cyclic carbonate **2g** in 83% yield (Table 1, Entry 16). Other silver salts could catalyze the incorporation reaction (Table 1, Entries 11–15), but silver cyanide produced a 38% yield and the starting propargylic alcohol was recovered (Table 1, Entry 10). The most efficient silver salts were silver methanesulfonate and silver acetate. They successfully catalyzed the conversion of **1g** into corresponding cyclic carbonate **2g** in high yields (Table 1, Entries 17 and 18). When the reaction was carried out in toluene under a CO_2 pressure of 1.0 MPa, the chemical yield improved up to 95% (Table 1, Entry 19).



Scheme 1. Proposed mechanism of CO_2 incorporation into propargylic alcohols.

Table 1. Examination of catalysts for the CO_2 incorporation reaction.[a]



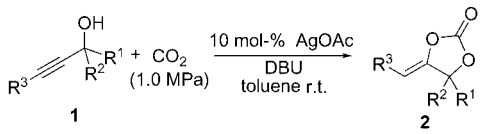
Entry	R	Metal salt	Yield [%][b]
1	Ph **1b**	$Rh(acac)_3$	no reaction
2		$Hg(OTf)_2$	no reaction
3		$PtCl_2$	no reaction
4		$PdCl_2$	no reaction
5		$Pd(OAc)_2$	trace
6		CuCl	trace
7		AuCl	no reaction
8		$AgClO_4$	quant.
9		AgOTs	quant.
10	$PhCH_2CH_2$ **1g**	AgCN	38
11		AgOTf	66
12		Ag_2CO_3	67
13		$AgBF_4$	67
14		AgF	68
15		$AgSbF_6$	77
16		$AgClO_4$	83
17		AgOMs	84
18		AgOAc	84
19[c]		AgOAc	95

[a] Reaction conditions: The reaction was carried out in dichloromethane (1.0 mL) with the metal salt (10 mol-%) as a catalyst, DBU (0.25 mmol), and the substrate (**1b** or **1g**, 0.25 mmol) under 2.0 MPa (for **1b**) or 1.0 MPa (for **1g**) CO_2 pressure. [b] Isolated yield. [c] The reaction was carried out in toluene.

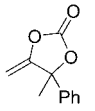
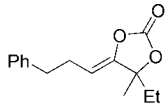
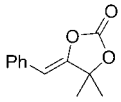
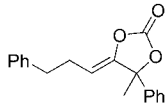
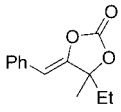
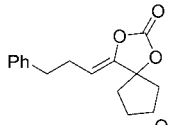
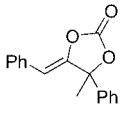
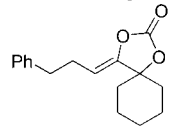
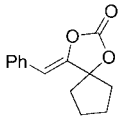
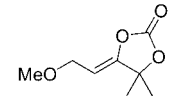
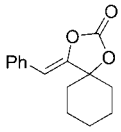
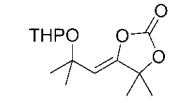
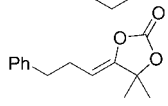
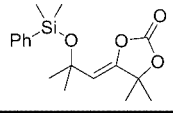
The combined catalytic system of silver acetate with a stoichiometric amount of DBU was successfully applied to various propargylic alcohols (Table 2). In the presence of 10 mol-% silver acetate and 1.0 equiv. of DBU[10] at room temperature, terminal alkyne **1a** possessing bulky substituents reacted with carbon dioxide and corresponding cyclic carbonate **2a** was obtained in an 85% yield (Table 2, Entry 1). Internal alkyne **1b** was quantitatively converted into cyclic product **2b** under atmospheric and 1.0 MPa CO_2 (Table 2, Entries 2 and 3). More bulky propargylic alcohols **1c** and **1d** were also smoothly converted into corresponding cyclic carbonates **2c** and **2d** in high yields, respectively (Table 2, Entries 5 and 6). The reaction of propargylic alcohol **1e** having a five-membered ring, or **1f** having a six-membered ring, smoothly proceeded in excellent yield (Table 2, Entries 8 and 10). The alkyl-substituted propargylic alcohols have never been reported to incorporate carbon dioxide, whereas in the present catalytic system, they were capable of reacting with CO_2 to afford cyclic carbonates **2g**–**k** in high yields (Table 2, Entries 12–16). It is noted that the propargylic alcohols with ether and acetal functions were smoothly converted into corresponding products **2l** and **2m**, respectively, in high yields without any loss of reactivity (Table 2, Entries 17 and 18). The silyl-protected propargylic alcohol was subjected to the present reaction conditions to obtain the cyclic carbonate with the silyl protected form **2n** in high yield (Table 2, Entry 19). Even under atmospheric pressure (0.1 MPa) of CO_2, propargylic alcohols **1b** and **1e**–**g** could be converted with excellent selectivity (Table 2, Entries 2, 7, 9, and 11), whereas other propargylic alcohols were not completely consumed, but they were converted into the corresponding product in high yield. The lower catalyst loading of 1.0 mol-% silver acetate also catalyzed the reaction of alcohol **1b** with 1.0 MPa of carbon dioxide to form carbonate **2b** in high yield (Table 2, Entry 4), though a longer time was needed to complete the reaction. The geometry of the carbon–carbon double bond in product **2k** was determined by X-ray analysis (Figure 1) to reveal that the (*Z*) isomer was obtained as the sole product.

Product **2b** was also found to have the (*Z*) form by comparing the chemical shift of the olefinic proton with the reported value.[3e] These observations suggested that a nucleophilic ring-closing step proceeded in an *anti* manner. All

Table 2. Various propargylic alcohols used for the incorporation of CO_2.[a]



1 2

Entry	Carbonate[g]		Yield / %[b]	Entry	Carbonate[g]		Yield / %[b]
1		**2a**	85	13		**2h**	quant
2[c]			quant				
3		**2b**	quant	14		**2i**	96
4[d]			98				
5		**2c**	quant	15		**2j**	95
6		**2d**	95	16		**2k**	96
7[c]		**2e**	80	17		**2l**	76
8			quant				
9[c]		**2f**	84	18		**2m**	97
10			96				
11[c]		**2g**	81	19		**2n**	91
12			95				

[a] Reaction conditions: The reaction was carried out in toluene (1.0 mL) with silver acetate (10 mol-%), DBU (0.25 mmol), and the substrate (0.25 mmol) under a CO_2 pressure of 1.0 MPa. [b] Isolated yield. [c] The reaction was carried out under atmospheric CO_2 pressure. [d] The reaction was carried out with silver acetate (1.0 mol-%) under a CO_2 pressure of 1.0 MPa. [e] The geometry of **2b** was (*Z*) by comparing the chemical shift with the reported value, see ref.[3e] [f] The geometry of **2k** was determined to be (*Z*) by X-ray analysis. [g] All the products were obtained as one isomer on the basis of ^{1}H NMR spectroscopic chemical shift data. Their geometries were suggested to be (*Z*) by NOE experiments.

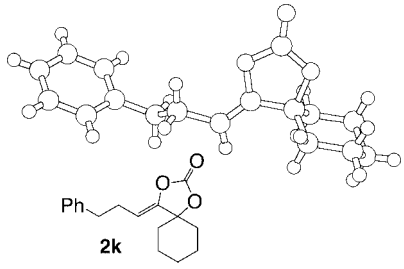


Figure 1. The structure of the CO_2-incorporated product.

other cyclic carbonates were obtained as a sole isomer by NMR spectroscopic analysis, and they were suggested to be the (*Z*) isomer by NOE experiments.

It is noted that the cyclization of carbon dioxide with propargylic alcohols proceeded stereoselectively by the combined use of a catalytic amount of a silver acetate and a stoichiometric amount of DBU. The silver–DBU catalytic system could be applied to a wide range of propargylic alcohols[11] to afford the corresponding CO_2-incorporated products in high chemical yields under mild reaction conditions. Further investigations are under way.

Experimental Section

Typical procedure: To a solution of propargylic alcohol **1g** (47.0 mg, 0.25 mmol) in toluene was added AgOAc (4.1 mg, 0.025 mmol) and DBU (38.0 mg, 0.25 mmol). The reaction mixture was stirred under 1.0 MPa CO_2 pressure for 5 h at room temperature. After the reaction was complete, the product was purified by silica gel column chromatography (EtOAc/hexane, 1:50). Corresponding carbonate **2g** was obtained in 95% yield as a colorless solid (m.p. 55.1–56.8 °C).

CCDC-635752 (for **2k**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for **2a**–**n** described in Table 2.

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[10] In principal, a catalytic amount of DBU is enough to drive the reaction, but we employed the stoichiometric amount of DBU to obtain good yields because the reactivity mainly depends on the substrates. When 10 mol-% of silver acetate and 10 mol-% of DBU were used, **2b** was obtained in 86% yield, whereas only a trace amount of **2g** was produced.

[11] Unfortunately, the present method was not applicable to primary or secondary propargylic alcohols for their conversion into the corresponding cyclic products.

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