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Silver Catalysis

C–C Bond Formation with Carbon Dioxide Promoted by a Silver Catalyst**

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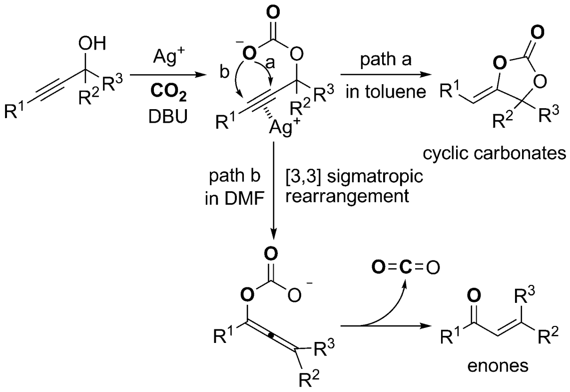
A range of chemical reactions have been reported to produce useful chemicals from carbon dioxide, which is an ubiquitous, abundant, cheap, and nontoxic C1 feedstock.[1] Carbon dioxide is also used in industry to generate some useful materials. However, carbon dioxide is thermodynamically stable and much less reactive than other carbon derivatives owing to its high oxidation state. Therefore, strong nucleophiles and harsh reaction conditions have been required when carbon dioxide is used in organic syntheses. For example, Grignard reagents[2] and organolithium compounds[3] are well known to react with carbon dioxide to afford the corresponding carboxylic acids. Transition-metal catalyzed reactions of carbon dioxide to produce the corresponding carboxylic acid and ester derivatives have also been reported. In these systems, however, a boron- or halogen-containing reactant must be prepared in advance, or a stoichiometric amount of another metal-containing reducing agent is required.[4] Several reactions of CO_2 that are catalyzed by metal complexes under harsh reaction conditions have been reported to afford more-stable products.[5] In some reactions, the esterification of products with alkyl halides is required for stabilization or purification and this process generates waste salts. The reaction of enolates with CO_2 to provide the corresponding β-ketocarboxylic acids is a promising C–C bond-forming reaction. However, the β-ketocarboxylic acid products are thermodynamically unstable, therefore only limited types of substrates could be used, as otherwise the product readily converts back into the starting substrate by decarboxylation.[6]

Recently, we reported that a silver catalyst could effectively act as a π-Lewis acid to activate the C–C triple bond in propargylic alcohols and thus promote the reaction of carbon dioxide in the presence of a base to afford the corresponding cyclic carbonates (Scheme 1, path a)[7] or the corresponding α,β-unsaturated carbonyl compounds (Scheme 1, path b);[8] the product obtained depended on the polarity of solvent.[9]

Based on X-ray analysis and NOE experiments, it was suggested that all cyclic carbonates possessed a *Z* olefin. Theoretical analysis of the silver catalytic system with *N*-methylpyrimidine as a model base revealed that the transition state would provide the *Z*-*exo*-alkene product.[9] Consequently, it was confirmed that the activation of the C–C triple bond by the silver catalyst, as a π-Lewis acid, was essential for these reactions. When the optically active Schiff base ligand for the silver catalyst was employed, symmetrical bispropargylic alcohols were converted into the cyclic carbonates through desymmetrization, in high yield and with high enantioselectivity.[9,10]



Scheme 1. Silver catalyst and DBU catalyzed the reaction of propargylic alcohol with carbon dioxide. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

In the reaction shown in Scheme 1, we believe the carbon dioxide would be captured by a hydroxy group to generate the carboxylate intermediate with formation of a new C–O bond. The resulting carboxylate could be trapped by the C–C triple bond, which had been activated by the silver catalyst, to afford the cyclic carbonate. Therefore, we postulated that when a ketone containing an alkyne group at an appropriate position is applied to the present reaction system, the derived enolate would capture carbon dioxide to generate the corresponding β-ketocarboxylate. The β-ketocarboxylate would then be trapped by the activated C–C triple bond to afford the corresponding stable lactone without the formation of any waste sideproducts (Scheme 2).[11] Herein, we report a catalytic C–C bond formation with carbon dioxide; this reaction involves C–C triple bond activation by a silver catalyst to afford the corresponding lactone under mild reaction conditions.

Several metal catalysts were initially investigated for the reaction of ketone **1a**, as the model substrate, in DMSO in the presence of DBU (2.0 equiv) under 1.0 MPa CO_2 pressure (Table 1). The reactions did not proceed in the absence of the metal salt (Table 1, entry 1). Palladium, copper, and gold(I) salts, which were expected to activate the C–C triple bond, hardly worked for this reaction (Table 1, entries 2–5). When a gold(III) salt was employed as the catalyst, the dihydrofuran

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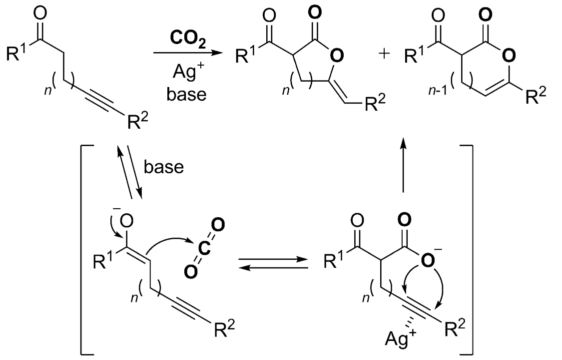
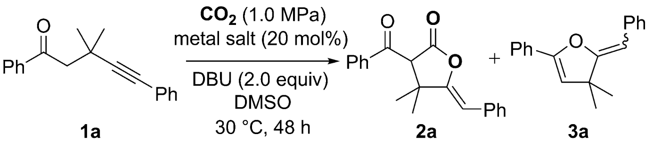


Scheme 2. The postulated reaction with carbon dioxide through C–C bond formation.

Table 1: Investigation of several metal salts.[a]



Entry	Metal Salt	Yield [%][b]	
		2a	**3a**
1	None	0	0
2	$Pd(OAc)_2$	trace	0
3	$Cu(OTf)_2$	0	0
4	AuCl	0	0
5	AuCl/AgOBz	0	0
6	$AuCl_3$	trace	13
7	AgOBz	40	5

[a] Reactions were carried out in 1.0 mL of solvent with 0.125 mmol of substrate **1a** under 1.0 MPa CO_2 pressure. [b] Yields of the isolated products. Bz = benzoyl, DMSO = dimethyl sulfoxide, Tf = trifluoromethanesulfonyl.

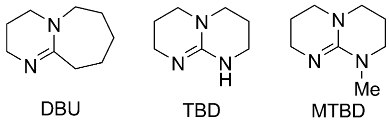
derivative **3a**,[12] which would be formed by the direct intramolecular cyclization of the enol derived from ketone **1a**, was obtained in 13% yield although the desired product was not obtained at all (Table 1, entry 6). Among the catalysts tested, a silver salt was the most effective catalyst for this reaction to produce the γ-lactone **2a** (Table 1, entry 7).[13]

Taking into account the acidity of the α proton of **1a**, several bases were screened (Table 2).[13] When DMAP was used the corresponding product **2a** was obtained in 6% yield (Table 2, entry 1), but when Hünig's base was used no product was formed (Table 2, entry 2). In the previous work, amidine-type bases such as DBU were effectively employed to afford the cyclic carbonates in high yield. These observations were supported by DFT calculations on the reactions.[9] Based on these results, various amine bases, such as TBD and MTBD, were examined. When MTBD was employed as a base (Table 2, entry 4), the product **2a** was obtained in good yield (48%), whereas TBD was not an effective base for this reaction (Table 2, entry 3). In the preliminary examination of solvents, nonprotic polar solvents were found to promote the reaction smoothly.[13] Several different nonprotic polar solvents were next examined (Table 2, entries 5–7). The reaction in DMI afforded product **2a** was in low yield, whereas the reaction in DMA gave the product **2a** in moderate yield (Table 2, entries 5, 6). Among the solvents examined, DMF was found to be the most suitable as the reaction in this solvent afforded the product **2a** in the highest yield (Table 2, entry 7). 4.0 equivalents of MTBD were sufficient to promote the reaction to afford the corresponding β-ketolactone **2a** in 89% yield (Table 2, entry 8).[13] At lower reaction temperatures the formation of the by-product furan **3a** was suppressed, thus the yield of **3a** decreased although a longer reaction time was required.[13] Under the optimized conditions the product **2a** was obtained in 91% yield at 25 °C in 48 h (Table 2, entry 9).

Table 2: Examination of various bases and solvents.[a]

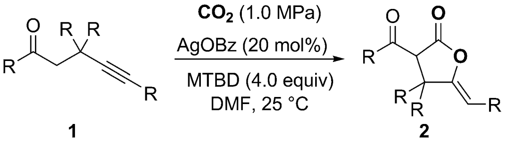
Entry	Base	Solvent	Yield [%][b]	
			2a	**3a**
1	DMAP	DMSO	6	–
2	$i Pr_2NEt$	DMSO	0	–
3	TBD	DMSO	7	–
4	MTBD	DMSO	48	6
5	MTBD	DMI	10	0
6	MTBD	DMA	59	4
7	MTBD	DMF	72	4
8	MTBD[c]	DMF	89	6
9[d]	MTBD[c]	DMF	91	4

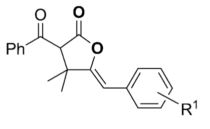
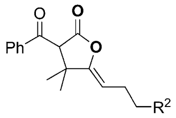
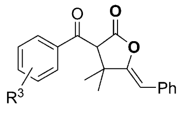
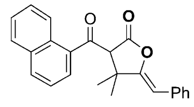
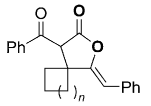
[a] Reactions were carried out in 1.0 mL of solvent with 0.125 mmol of substrate **1a** in the presence of AgOBz (20 mol%) and 2.0 equivalents of base under 1.0 MPa CO_2 pressure. [b] Yields of the isolated products. [c] 4.0 equivalents of MTBD were used. [d] The reaction was performed at 25 °C. DMI = 1,3-dimethyl-2-imidazolidinone, DMA = *N*,*N*-dimethylacetamide.



The substrate scope of this reaction was investigated under the optimized catalytic reaction conditions (Table 3). Initially the reactions of substrates that were derived from acetophenone and had a range of alkyne substituents were examined (Table 3, entries 1, 3–8). The reactions of substrates having phenyl (**1a**), *p*-tolyl (**1b**), *m*-methoxyphenyl (**1c**), *p*-fluorophenyl (**1d**), and *p*-trifluoromethylphenyl (**1e**) groups on the alkyne proceeded under the optimized reaction conditions to achieve high yields, irrespective of the electron-withdrawing or electron-donating nature of the group on the phenyl ring. When the catalyst loading was decreased to from 20 mol% to 10 mol%, the reaction of ketone **1a** with carbon dioxide gave the lactone **2a** in good yield (Table 3, entry 2), although a longer reaction time was needed for the reaction to go to completion.[13] The reaction of substrates **1f** and **1g**, which bear an alkyl substituent on the alkyne, were also catalyzed in the presence of 6.0 equivalents of MTBD to afford the corresponding product **2f** and **2g** in good yields (Table 3, entries 7 and 8) under 2.0 MPa CO_2 pressure. Substrates derived from aromatic ketones were subjected to this catalytic system under the optimized reaction conditions (Table 3, entries 9–14). The *p*-tolyl ketone derivative **1h** was

Table 3: AgOBz and MTBD system was applied to the reaction of several substrates (**1a**–**1o**).[a]

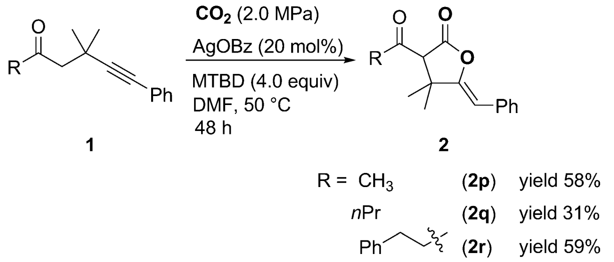


Entry	Product			*t* [h]	Yield [%][b]
1		$R^1 =$	H (**2a**)	48	91
2[c]			H (**2a**)	240	85
3			*p*-Me (**2b**)	96	90
4			*m*-MeO (**2c**)	96	87
5			*p*-F (**2d**)	72	79
6			*p*-CF_3 (**2e**)	48	90
7[d]		$R^2 =$	Ph (**2f**)	70	77
8[d]			CH_2CH_3 (**2g**)	72	83
9		$R^3 =$	*p*-Me (**2h**)	72	84
10[e]			*p*-CF_3 (**2i**)	192	79
11[f]			*p*-MeO (**2j**)	144	69
12[f,g]			*m*-MeO (**2k**)	144	77
13[f,g]			*o*-MeO (**2l**)	220	76
14[d]			(**2m**)	120	77
15[h]			*n* = 1 (**2n**)	120	74
16[h,i]			*n* = 2 (**2o**)	48	36[j]

[a] The reaction was performed with AgOBz (20 mol%) and MTBD (4.0 equiv) in 1.0 mL of DMF with 0.125 mmol of substrate **1** at 25 °C under 1.0 MPa CO_2 pressure. [b] Yield of the isolated products. [c] The amount of silver catalyst was decreased from 20 mol% to 10 mol%. [d] The reaction was carried out with 6.0 equivalents of MTBD under 2.0 MPa CO_2 pressure. [e] The reaction temperature was 5 °C. [f] The reaction was performed at 10 °C under 2.0 MPa CO_2 pressure. [g] AgOBz (40 mol%) was used. [h] The reaction was carried out under 2.0 MPa CO_2 pressure. [i] AgOAc (40 mol%) was used instead of AgOBz at 60 °C. [j] 47% of ketone **1o** was recovered and the corresponding furan was obtained in 6% yield.

a good substrate for this reaction and the corresponding product **2h** was obtained in good yield (Table 3, entry 9). The substrate bearing a *p*-trifluoromethylbenzoyl group **1i** was also a good substrate, producing the corresponding product **2i** in good yield, although a longer reaction time and low reaction temperature were required (Table 3, entry 10). This catalytic system catalyzed reaction of methoxy-substituted ketone derivative **1j**, but the yield was not satisfactory. The yield of the product **2j** was improved to 69% at lower temperature (10 °C) under 2.0 MPa CO_2 pressure (Table 3, entry 11). The reactions of other methoxyacetophenone derivatives **1k** and **1l** proceeded in the presence of AgOBz (40 mol%) at 10 °C under 2.0 MPa CO_2 pressure and the corresponding products (**2k** and **2l**) were obtained in good yields (Table 3, entries 12–13). The 1-naphtyl derivative (**1m**) was transformed into the corresponding lactone derivative (**2m**) in 77% yield when 6.0 equivalents of MTBD were used (Table 3, entry 14). The ketone having a cyclobutyl substituent (**1n**) was also converted efficiently into the corresponding product (**2n**) in good yield under the same catalytic system with 2.0 MPa CO_2 pressure (Table 3, entry 15). The substrate bearing a cyclopentyl group (**1o**) was also applied to this catalytic system and the product (**2o**) was obtained in 36% yield (Table 3, entry 16).

The present catalytic system was also applied to aliphatic ketone derivatives (**1p**, **1q**, and **1r**; Scheme 3) at 50 °C under 2.0 MPa CO_2 pressure. Substrate **1p** was converted into the corresponding γ-lactone **2p** in 58% yield. The yield of γ-lactone **2q** was not satisfactory (31% yield), but the reaction of ketone **1r** with carbon dioxide afforded the corresponding γ-lactone **2r** in 59% yield. These ketones possess two different protons α and α′ to the carbonyl group and thus two different enolates can be generated, but the γ-lactone was selectively obtained without the formation of any other lactone derivatives. The reaction to form the five-membered lactone is the productive pathway,[13] and the corresponding γ-lactone was selectively obtained without any need for control of the enolization.



Scheme 3. The reaction of aliphatic ketone derivatives (**2p**–**2r**).[14] DMF = *N*,*N*-dimethylformamide.

The geometry of the C–C double bond in the lactone derivative **2h** was confirmed by X-ray analysis to reveal the *Z* isomer as the sole product (Figure 1). All other lactone derivatives were also selectively obtained as the *Z* isomers based on NOE experiments.

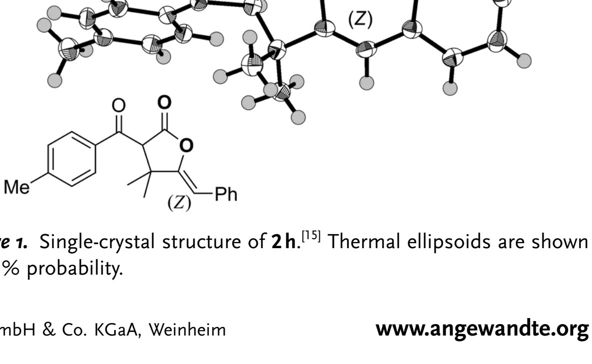


Figure 1. Single-crystal structure of **2h**.[15] Thermal ellipsoids are shown at 50% probability.

In this study, we successfully developed a catalytic C–C bond-forming reaction with carbon dioxide; this reaction employed catalytic silver benzoate in the presence of MTBD to afford lactone derivatives in good-to-high yields under mild reaction conditions. This reaction system could be applied to aliphatic ketone derivatives and the corresponding lactone was obtained without any control of the formation of enolate. The geometry of the C–C double bond of the products was confirmed to be *Z* based on X-ray analysis and NOE experiments. Further applications of the silver-catalyzed C–C bond-forming reaction with carbon dioxide are underway with various organic compounds.

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Keywords: carbon dioxide · C–C bond formation · homogeneous catalysis · silver · synthetic methods

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[11] This hypothesis was based on the theoretical study of the reaction of propargylic alcohol with carbon dioxide, see Ref. [9].

[12] It was reported that the dihydrofuran derivatives were formed in the presence of an acid catalyst at high temperature. See: Z. P. Zhan, S. P. Wang, X. B. Cai, H. J. Liu, J. L. Yu, Y. Y. Cuia, *Adv. Synth. Catal.* **2007**, *349*, 2097–2102.

[13] See the Supporting Information.

[14] The other products were furan derivatives and the recovered starting ketone **1**.

[15] CCDC 827765 (**2h**) 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.