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Communication

Thermodynamic favorable CO₂ conversion *via* vicinal diols and propargylic alcohols: A metal-free catalytic method

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ABSTRACT

Organocatalysis represents a promising field in chemical fixation of CO₂. Herein, a facile metal-free strategy was reported for the one-pot preparation of cyclic carbonates and α -hydroxy ketones from vicinal diols, propargylic alcohols and CO₂. Wide scope of vicinal diols and propargylic alcohols was demonstrated to be efficient under the DBU-catalyzed conditions. A plausible mechanism was proposed, which included detailed main and side reactions under the metal-free conditions.

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Recently, more and more attention was paid to CO₂ utilizing as green C₁ building block in organic synthesis due to its good features such as abundance, nontoxicity and renewability [1–4]. Up to now, several useful products from CO₂ as C₁ feedstock, e.g., urea, salicylic acid, organic carbonates, methanol and polycarbonates on a large scale have been produced in the chemical industry which consumed approximately 116 million tons of CO₂ per year [5]. Nevertheless, the chemical varieties are limited which results from the hindrance by the efficiency and economic respects. Therefore, to utilize CO₂ in an effective and low-cost manner will be of great significance and urgently required.

Due to the thermodynamic stability and kinetic inertness of CO₂ molecule, the activation of CO₂ is indispensable by the highly active species in the transformation [6,7]. In the previous studies, most of the effective catalytic systems still depended on the transition metal catalysis [8,9]. Most of the active metal complexes were thermolabile and sensitive to air/water. In addition, much attention was paid to the organocatalysis because of its cheap, nontoxic, easily tunable skeleton and multiple functional sites features [10,11]. It also represented a forceful tool to effectively activate CO₂ molecule and promote its conversion under mild reaction conditions. In the reported works, many transformations on CO₂ through organocatalysis manner were achieved such as *N*-heterocyclic carbene [12–15], *N*-heterocyclic olefin [16,17],

frustrated Lewis pairs [18–21], superbases [22–24], task-specific ionic liquids [25–27] and others [24,28–30].

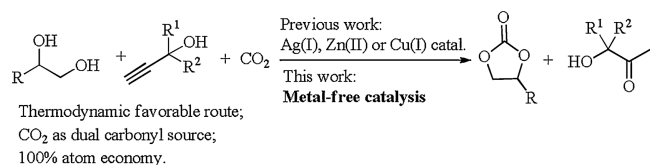
Three-component cascade reaction of propargylic alcohols, CO₂ and vicinal alcohols provided a thermodynamically favorable access to cyclic carbonates and α -hydroxyl ketones [31]. In the process, CO₂ acted as both carbon and oxygen source for carbonyl group construction with 100% atom economy. Reported systems were based on transition metals such as Ag(I) [31,32], Cu(I) [33], and Zn(II) [34] (Scheme 1), and the study of organocatalysis on the process has not been involved.

Among the organocatalysis, strong base was revealed for its good properties such as easily available material and rich electronegativity which was beneficial for the activation of CO₂ [35,36] and hydroxyl [37,38] through strong hydrogen bond interaction. On the basis of the theory, we proposed that the amidine base could be the potential catalyst to effectively promote the cascade reaction of propargylic alcohols, CO₂ and vicinal alcohols to cyclic carbonates and α -hydroxyl ketones. Delightedly, herein, metal-free catalysis for the three-component reaction was disclosed to produce cyclic carbonates and α -hydroxyl ketones with satisfactory yields of products (Scheme 1).

We thus started to explore the practicability of the proposed conjugated strong base-promoted method in Scheme 1. Initially, a reaction of propylene glycol **1a**, propargylic alcohol **2a**, and CO₂ in CH₃CN under the given conditions was investigated (Table 1). To our delight, when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was employed as the catalyst, the corresponding products, *i.e.*, propylene carbonate (PC, **3a**) and α -hydroxy ketone **4a** were obtained in 61% and 58% yields, respectively (entry 1). At the same time, several

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Scheme 1. Thermodynamically favorable cascade reaction for CO₂ conversion.

Table 1

The effect of different basic catalysts and solvents on the synthesis of **3a** and **4a**.^a

Entry	Catalyst	Solvent	3a Yield (%) ^b	4a Yield (%) ^b
1	DBU	CH ₃ CN	61	58
2	DBN	CH ₃ CN	57	61
3	TBD	CH ₃ CN	38	41
4	TMG	CH ₃ CN	35	36
5	K ₂ CO ₃	CH ₃ CN	7	11
6	Cs ₂ CO ₃	CH ₃ CN	9	14
7	Et ₃ N	CH ₃ CN	2	5
8	DBU	neat	20	44
9	DBU	DMF	73	71
10	DBU	DMSO	69	63
11	DBU	CH ₂ Cl ₂	12	9

^a Reaction conditions: **1a** (76.1 mg, 1 mmol), **2a** (84.1 mg, 1 mmol), catalyst (0.5 mmol), solvent (2 mL), CO₂ 1 MPa, 120 °C, 10 h.

^b Determined by GC using biphenyl as the internal standard. **3a** yield is based on **1a**, and **4a** yield is based on **2a**.

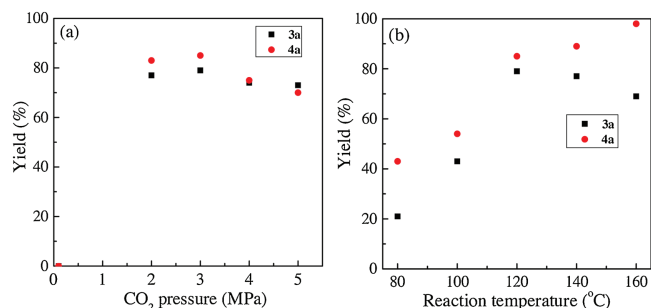


Fig. 1. Effect of (a) CO₂ pressure and (b) reaction temperature on the product yields. Reaction conditions: **1a** (76.1 mg, 1 mmol), **2a** (84.1 mg, 1 mmol), DBU (76.0 mg, 0.5 mmol), DMF (2 mL), 10 h. (a) 120 °C; (b) CO₂ (3 MPa). The yield was determined by GC using biphenyl as the internal standard. **3a** yield was based on **1a**, and **4a** yield was based on **2a**.

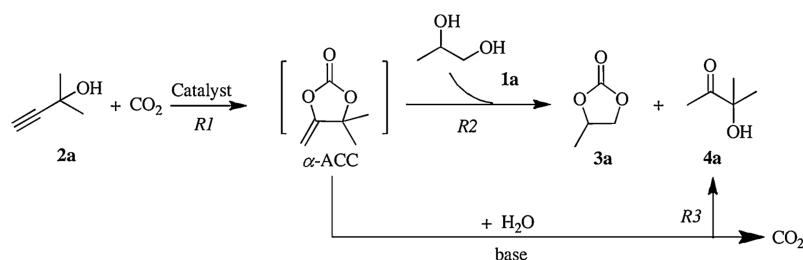
typical guanidine bases were also examined as catalyst. As seen from the results (entries 2–4), they also showed catalytic activity for the transformation. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)

possessing the similar structure with DBU gave the equivalent level result (entry 2). The other strong base such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,1,3,3-tetramethylguanidine (TMG) gave lower yields (entries 3 and 4). As we all know, the basicity strength of the catalyst plays a key role in the coupling reaction of CO₂ and propargylic alcohol, which is the rate-determining step in the three-component reaction [32,39]. Generally, the weak basicity of catalysts resulted in low activity, while the strong base exhibited a higher conversion and a lower yield because of some side reactions [38]. The basicity of the guanidine bases (entries 1–4) followed the order: TBD > DBN > DBU > TMG [39–41]. However, their catalytic activity showed as DBU, DBN > TBD > TMG, an action from both basicity and nucleophilicity indicating a good agreement with the previous works [38,42]. Additionally, both K₂CO₃ and Cs₂CO₃ led to the lower yields (entries 5 and 6). The unconjugated base, *i.e.*, Et₃N exhibited significantly a lower catalytic activity than that of guanidine bases (entries 7 vs. 1–4). Clearly, the guanidine bases displayed better performance than that of the other basic catalysts.

Furthermore, the reactions in different solvents were explored in the presence of DBU, and the results revealed the obvious influence of the medium. The use of DMF as the solvent gave a higher yield than that of CH₃CN, dimethyl sulfoxide (DMSO) or CH₂Cl₂ (entries 9 vs. 1, 10 and 11). In addition, the reaction worked with less efficiency under the solvent-free conditions (entry 8).

Next, the effect of CO₂ pressure on the reaction was tested, and the results were shown in Fig. 1a. No target product was detected under the atmospheric pressure. However, the yield of product obviously increased when CO₂ pressure was from 2 to 5 MPa. Especially, the best result was obtained under 3 MPa, and the yields of **3a** and **4a** were 79% and 85%, respectively. Notably, due to the formation of carbonic acid from high pressure CO₂ and trace water in the reaction system, the activity of the strong base DBU might be weakened [43,44]. As a result, a slightly lower product yield was obtained in 4 MPa and 5 MPa CO₂. As shown in Fig. 1b, reaction temperature had a great influence on the process. **4a** yield was continually increased from 43% to 98% with the increase of temperature. Nevertheless, a decline of **3a** yield occurred when the temperature was higher than 120 °C. Clearly, 120 °C was the optimized reaction temperature.

According to the reported works [31,34], this three-component reaction proceeded with a sequential carboxylation and cyclization of propargylic alcohol and CO₂ (*R1*, Scheme 2), and interesterification between intermediate α -alkylidene cyclic carbonate (α -ACC) and 1,2-diol (*R2*) with the generation of cyclic carbonate and α -hydroxyl ketone. In addition, α -ACC was easily hydrolyzed to α -hydroxyl ketone in a basic condition (*R3*). Therefore, there was a competitive relationship between *R2* and *R3*. As seen from Fig. 1b, increase temperature from 80 °C to 120 °C narrowed the gap in yield between **4a** and **3a**. Presumably, although the reaction rates of *R2* and *R3* were both accelerated with increasing temperature, *R2* was signally promoted in the presence of the strong base DBU. In contrast, further increase in temperature led to a weaker



Scheme 2. The procedure of the three-component cascade reaction.

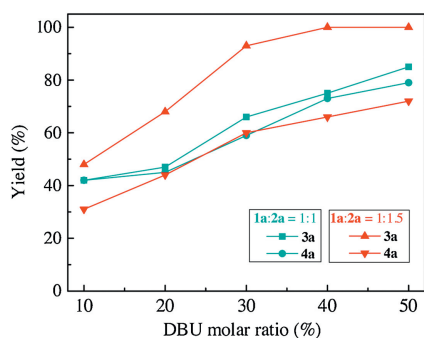


Fig. 2. Dependence of the yield on amount of DBU. Reaction conditions: **1a** (76.1 mg, 1 mmol), **2a** (84.1 mg, 1 mmol)/(126.2 mg, 1.5 mmol), DMF (2 mL), CO₂ (3 MPa), 120 °C, 10 h. The yield was determined by GC using biphenyl as the internal standard. **3a** yield was based on **1a**, and **4a** yield was based on **2a**.

catalytic activity, and the reaction rate of **R3** was faster than that of **R2**. Accordingly, the yield of **4a** was getting higher than that of **3a** from 120 to 160 °C. Additionally, an increased CO₂ pressure might inhibit **R3**, leading to the decreased yield of **4a** (Fig. 1a).

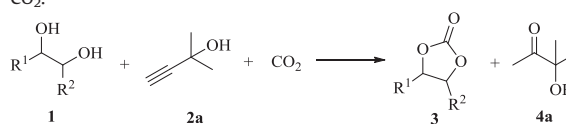
Fig. 2 showed the relationship between product yields and the amount of DBU. Based on the above conditions, increase the amount of DBU was found to be effective in facilitating the reaction process. However, both yields of **3a** and **4a** did not exceed 85%. However, further addition of **2a** (molar ratio up to 1.5) greatly enhanced the catalytic efficiency, and **4a** yield was up to 100% with 40 mol% DBU. These results indicated that increase the amount of propargylic alcohol in the catalytic system could promote **R1** and further accelerate **R2**.

With the optimized reaction conditions in hand, the substrate scope was explored with 1.5 equiv. of propargylic alcohol at 120 °C under 3 MPa CO₂ using 40 mol% of DBU as the catalyst in DMF for 10 h. As shown in Table 2, a series of vicinal diols were demonstrated to be effective under the identical conditions. The vicinal diols bearing different linear alkyl reacted with propargylic alcohol **2a** and CO₂, and gave cyclic carbonates **3a–d** and α -hydroxy ketone **4a** in almost quantitative yields (entries 1–4). The aryl-substituted diol and 1,2-cyclohexanediol showed a slight lower reactivity than that of alkyl-substituted diols, which indicated the influence of electronic and steric effect (entries 5 and 6). What is more, glycerol was also tested, and the target product, *i.e.*, glycerol carbonate **3g** was obtained in excellent yield (entry 7). 1,2,6-Hexanetriol was found to be effectively transformed into **3h**, but its yield was lower than that of other carbonates (entry 8).

Next, we examined the effect of propargylic alcohols on the reaction (Table 3). As shown, all alkyl substituted propargylic alcohols could react with CO₂ and **1a** (entries 1–4), but a slightly lower yield was obtained when there was a large substituent group, such as isobutyl (entry 3) and cyclohexyl (entry 4). The reason might be due to the steric effect. Gratifyingly, the catalytic system worked well for the aryl- or vinyl-substituted propargylic alcohol (entries 5 and 6). In addition, it was found that the corresponding product **4g** was also obtained in moderate yield when secondary alcohol was used as a substrate (entry 7).

On the basis of previous reports [31,32,35–37,45], a possible mechanism is proposed in Scheme 3. The first step is the carboxylation of activated propargylic alcohols with DBU–CO₂ adduct along with the formation of the intermediate **A**. An intramolecular ring-closing reaction of **A** will proceed and afford α -ACCs (This intermediate was demonstrated by control experiments in Scheme S1, Supporting information). Then, 1,2-diols nucleophilic attack α -ACCs to form intermediate **B**, which subsequently transforms into intermediate **C**. Finally, cyclic carbonates and α -hydroxyl ketones are simultaneously obtained

Table 2
Scope investigation for the reaction of vicinal diols **1**, propargylic alcohol **2a**, and CO₂.^{a,b}



Entry	Sub. 1	Prod. 3	Yield (%)	
			3	4a
1			99	66
2			99	65
3			>99	54
4			>99	59
5			91	49
6			95	55
7			97	63
8			32	26

^a Reaction conditions: **1** (1 mmol), **2a** (126.2 mg, 1.5 mmol), DBU (60.8 mg, 0.4 mmol), DMF (2 mL), CO₂ (3 MPa), 120 °C, 10 h, **3** yields are based on **1**, and **4a** yield is based on **2a**.

^b GC yield.

through intramolecular nucleophilic cyclization of intermediate **C**. Notably, hydrolysis of α -ACCs with trace water in a basic condition also generates α -hydroxyl ketones, which competes with main reaction.

In summary, an efficient strategy for the synthesis of cyclic carbonates and α -hydroxy ketones through a three-component reaction of vicinal diols, propargylic alcohols, and CO₂ in the presence of DBU catalyst has been developed. The resource utilization of CO₂ through easily available vicinal diols and propargylic alcohols works efficiently. Through the activation of CO₂ and substrates, the desired cyclic carbonates and α -hydroxy ketones are generated in good yield and selectivity. The mechanism revealed the main and side processes under the metal-free conditions.

Table 3
Scope investigation for the reaction of propylene glycol **1a**, propargylic alcohol **2**, and CO₂.^{a,b}

Entry	Sub. 2	Prod. 4	Yield (%)	
			3a	4
1			99	66
2			80	57
3			65	57
4			49	42
5			91	94
6			83	56
7			56	47

^a Reaction condition: **1a** (76.1 mg, 1 mmol), **2** (1.5 mmol), DBU (60.8 mg, 0.4 mmol), DMF (2 mL), CO₂ (3 MPa), 120 °C, 10 h, **3a** yield is based on **1a**, and **4** yields are based on **2**.

^b GC yield.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2019.06.030>.

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