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Synthesis of Unsymmetrical Organic Carbonates using CO_2 as a Feedstock in AgCl/Ionic Liquid System at Ambient Conditions

Jiayin Hu[1,2], Jun Ma[1]*, Lu Lu[1,2], Qingli Qian[1], Zhaofu Zhang[1], Chao Xie[1,2], Buxing Han[1,2]*

Abstract: Synthesis of unsymmetrical organic carbonates from the renewable and cheap CO_2 is of great importance, but is challenging, especially at ambient conditions. In this work, we found that some metal salt/ionic liquid catalyst systems were highly active for the synthesis of unsymmetrical organic carbonates from CO_2, propargylic alcohols, and primary alcohols. Especially, AgCl/1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) system was very efficient for the reactions of a wide range of substrates at room temperature and atmospheric pressure, and the yields of the unsymmetrical organic carbonates could approach 100%. The catalyst system could be reused at least five times without changing the catalytic performance, and could be easily recovered and reused. Detailed study indicated that AgCl and [Bmim][OAc] catalyzed the reactions cooperatively, resulting in unique catalytic performance.

Introduction

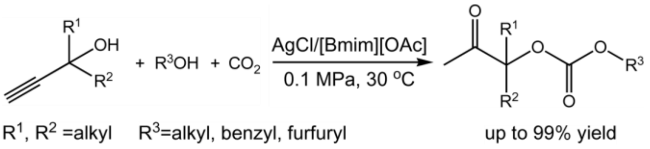
Transformation of carbon dioxide (CO_2) into value-added bulk and fine chemicals is an important topic in green chemistry because CO_2 is an abundant, nontoxic, and renewable carbon resource.[1] So far, CO_2 has been successfully transformed into various chemicals, such as organic carbonates,[2] polymers,[3] N-containing derivatives,[4] formic acid,[5] alcohols[6] and others. Transformation of CO_2 under mild reaction conditions, especially at atmospheric pressure and room temperature, is interesting both in academia and industry.[7] However, because CO_2 is thermodynamically stable and kinetically inert,[8] its conversion, especially at ambient conditions is challenging.

Organic carbonates are important intermediates in the synthesis of fine chemicals and pharmaceuticals.[9] They have also been utilized as polar aprotic solvents in nonaqueous Li-O_2 batteries,[10] synthetic lubricants and plasticizers, mild carbonylation or methylation agents to replace poisonous phosgene and dimethyl sulfate,[11] and monomers for organic glasses.[12] Compared to symmetrical organic carbonates, unsymmetrical organic carbonates are more useful,[13] but the synthetic routes are more complex and toxic chemicals, such as phosgene, pyridine and carbon monoxide, are often used.[14] The reaction of CO_2 and propargylic alcohols could synthesize unsymmetrical organic carbonates catalyzed by N-heterocyclic carbenes.[15] Costa and co-workers reported that unsymmetrical organic carbonates could be synthesized from CO_2, propargylic alcohols, and primary alcohols at high temperature (100 ºC) and high pressure using superbase (1,3,4,6,7,8-hexaydro-1-methyl-2H-pyrimido[1,2-α]pyrimidine) as catalyst, and the highest yield of carbonate was 87%.[16] Very recently, Ag_2CO_3/PPh_3 system was used to catalyze the reaction of CO_2, benzyl alcohol and equimolar 2-methylbut-3-yn-2-ol at 80 ºC and 2 MPa CO_2 pressure in CH_3CN, and the highest yield of carbonate was 84%.[17]

Ionic liquids (ILs) have some very attractive properties, such as negligible vapor pressure and nonflammability.[18] ILs have also been used widely as catalysts to promoted organic reactions.[19] Moreover, ILs are not only excellent solvents for organic substances, but also for inorganic transition metal salts.[20] Metal salt/IL systems usually have characteristics of ILs and metal salts.[21]

Results and Discussion

In this work, we found that AgCl/1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) catalyst system was very efficient for the synthesis of unsymmetrical organic carbonates from CO_2 and propargylic alcohols in the presence of primary alcohols under atmospheric CO_2 pressure and room temperature (Scheme 1). In the reaction, the AgCl/IL system acted as both catalyst and solvent, which avoided the use of volatile organic solvents. In addition, the catalyst system could be easily reused with excellent stability. As far as we know, this is the first work to conduct this kind of reactions at ambient temperature and pressure with satisfactory efficiency.



Scheme 1. The reaction of CO_2, propargylic alcohols, and primary alcohols to synthesize unsymmetrical organic carbonates.

Various catalysts were tested using 2-methyl-3-butyn-2-ol (**1a**) and methanol (**2a**) as the substrates at room temperature and 0.1 MPa CO_2, and the results are given in Table 1. The reaction did not occur without catalyst (Table 1, entry 1). The individual catalyst AgCl or [Bmim][OAc] was not active under the given conditions (Table 1, entries 2-3). The catalytic activity of

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J.Hu[1,2], J. Ma[1]*, L. Lu[1,2], Q. Qian[1], Z. Zhang[1], C. Xie[1,2], Prof. B. Han[1,2]*

[1] Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Colloid and Interface and Thermodynamics Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[2] School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
Tel. /Fax: (+86) 010-62562821
E-mail: majun@iccas.ac.cn; hanbx@iccas.ac.cn

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CuCl/[Bmim][OAc] and $ZnCl_2$/[Bmim][OAc] were also screened (Table 1, entries 4-5), and the yields of the target product methyl 2-methyl-3-oxobutan-2-yl carbonate (**3a**) were 43% and 0%, respectively. In addition, the catalyst activity of reported Ag_2CO_3/PPh_3 system with 20% molar ratio was also studied at ambient conditions in CH_3CN in 6 h, and the yield of **3a** was only 2%. Subsequently, various silver salts including $AgBF_4$, $AgNO_3$, AgOTf, AgOAc, Ag_2CO_3 and AgCl were respectively combined with [Bmim][OAc], and the homogeneous systems were used as both the catalysts and solvents for the reaction. Interestingly, all the Ag salt/IL catalysts were active for the reaction (entries 6-10, 18). Among them, AgCl/[Bmim][OAc] showed the highest activity with >99% yield of **1a** within 6 h (entry 18). The catalytic performances of ILs with different cations and anions were studied (entries 11-18). AgCl/1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) system, in which the IL is neutral, was not active for the reaction (entry 11). The yield of **3a** was 6% and 13% respectively when Ag_2CO_3/[Bmim][Cl] and AgOAc/[Bmim][Cl] were used as catalysts, but they were not as active as AgCl/[Bmim][OAc].The catalytic activity of AgCl/1-butyl-3-methylimidazolium imidazolide ([Bmim][Im]) system with IL of strong basicity[22] was very low (entry 14). All the ILs with acetate anion ($[OAc]^-$), 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]), 1-octyl-3-methylimidazolium acetate ([Omim][OAc]), 1-butyl-2,3-dimethylimidazolium acetate ([Bmmim][OAc]) and [Bmim][OAc], were very effective for the reaction (entries 15-18). The results suggest that the $[OAc]^-$ of ILs is crucial for the high catalytic activity.

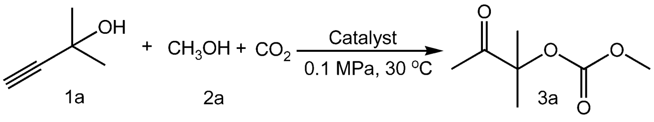


Table 1. Reaction of CO_2, 2-methyl-3-butyn-2-ol (**1a**) and methanol (**2a**) in various catalyst systems.[a]

Entry	Catalyst		Y[b] (%)
	Metal Salt	IL	
1	--	--	0
2	AgCl	--	0
3	--	[Bmim][OAc]	0
4	CuCl	[Bmim][OAc]	43
5	$ZnCl_2$	[Bmim][OAc]	0
6	$AgBF_4$	[Bmim][OAc]	61
7	$AgNO_3$	[Bmim][OAc]	68
8	AgOTf	[Bmim][OAc]	79
9	AgOAc	[Bmim][OAc]	92
10	Ag_2CO_3	[Bmim][OAc]	97
11	AgCl	[Bmim][Cl]	0
12	Ag_2CO_3	[Bmim][Cl]	6
13	AgOAc	[Bmim][Cl]	13
14	AgCl	[Bmim][Im]	19
15	AgCl	[Emim][OAc]	97
16	AgCl	[Omim][OAc]	94
17	AgCl	[Bmmim][OAc]	95
18	AgCl	[Bmim][OAc]	>99
19[c]	AgCl	[Bmim][OAc]	99

[a] Reaction conditions: **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0481 g), IL (1.5 mmol), metal salt (0.3 mmol), CO_2 (0.1 MPa), 30 °C, 6 h. [b] The yield was determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard. [c] **1a** (6.0 mmol, 0.5047 g), **2a** (6.0 mmol, 0.1923 g), [Bmim][OAc] (6.0 mmol, 1.1896 g), AgCl (1.2 mmol, 0.1724 g), CO_2 (0.1 MPa), 30 °C, 6 h.

The results above showed that AgCl/[Bmim][OAc] catalyst system could promote the reaction effectively at room temperature and atmospheric pressure. We studied the effect of [Bmim][OAc] amount on the reaction, and the results are given in Figure 1. The yield of **3a** increased with the increase of [Bmim][OAc] amount. The yield of **3a** was much lower when catalytic amount of [Bmim][OAc] was tested. One of the main reasons was that AgCl could not be dissolved completely to form a homogeneous system. The results suggested that the IL [Bmim][OAc] acted as both catalyst and solvent.

The effect of AgCl content and reaction time on the reaction over the catalyst system were also tested, and the results are given in Figure 2. The yield of **3a** increased with the increasing content of the AgCl (Figure 2a). Figure 2b showed that the yield of **3a** increased with increasing reaction time and could reach 100% in 24 h when 5% AgCl was used. The times to reach 100% yields were 6 h and 24 h respectively as the contents of AgCl were 20 mol% and 5 mol% of the substrate. The catalyst system was very effective considering that the reaction was carried out at ambient condition, which has not been realized by other catalysts. The reusability of AgCl/[Bmim][OAc] was tested using catalyst system with 20 mol% AgCl, and the results are shown in Figure 3. The catalytic activity and selectivity of the catalyst system did not change notably after being reused five times. After 5 times of recycle, the IL in the catalyst system was extracted by H_2O, and then was characterized by NMR after removing H_2O under vacuum. The ^1H NMR and ^{13}C NMR spectra of the reused IL (Supporting Information) demonstrated that the IL maintained the same structure as the virgin one, which is consistent with excellent reusability.

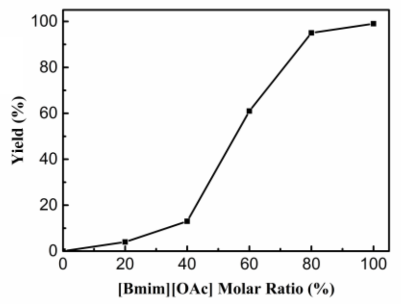


Figure 1. Dependence of the yield on amount of [Bmim][OAc] with different [Bmim][OAc] contents. Reaction conditions: **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0481 g), AgCl (0.3 mmol, 0.0431 g), CO_2 (0.1 MPa), 30 °C, 6 h, different [Bmim][OAc] contents. The yield was determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

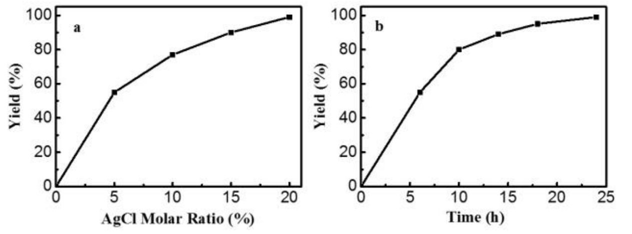


Figure 2. Reaction conditions: **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0481 g), [Bmim][OAc] (1.5 mmol, 0.2974 g), CO_2 (0.1 MPa), 30 ºC, different AgCl contents and different reaction times, respectively. The yield was determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard. a: Dependence of the yield on amount of AgCl with different AgCl contents in 6 h. b: The time profiles of the conversion of **1a** by 5% AgCl catalyst with different reaction times.

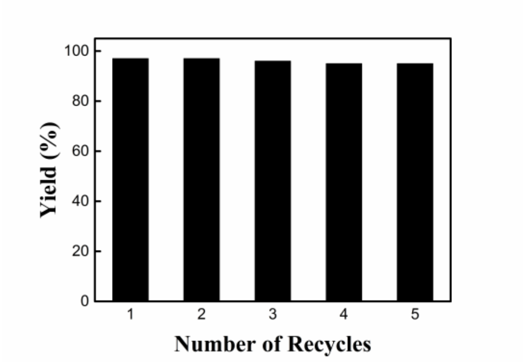


Figure 3. Recyclability of the AgCl/[Bmim][OAc] system. Reaction conditions: **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0481 g), [Bmim][OAc] (1.5 mmol, 0.2974 g), AgCl (0.3 mmol, 0.0431 g), CO_2 (0.1 MPa), 30 ºC and 6 h

The reactions of atmospheric pressure CO_2 with a range of different substituted substrates were then conducted in the AgCl/[Bmim][OAc] catalyst system. The optimized reaction times, the ^1H NMR spectroscopy yields and the isolated yields are summarized in Table 2. We began with examining the effect of varying propargylic alcohols of the reaction. In general, propargylic alcohols with different alkyl substituents at the propargylic position were effective substrates to give the corresponding carbonates **3a-3d** in excellent yields. It appears that the reaction is sensitive to the sterically hindered effect of substituted R^1 and R^2. When R^1 was methyl and R^2 was methyl or ethyl, the substrates could be completely converted within 6 h (**3a-3b**), As R^1 and R^2 were alkyls with much stronger sterically hindered effects, a much longer time was needed to complete the reaction (**3c-3d**). Next, we examined the effect of primary alcohols on the reaction (**3a, 3e-3h**). With the increase of alkyl chain length, a longer time was needed to complete the reaction (**3a, 3e, 3f**). In addition, the primary alcohols with benzyl and furfuryl were also studied, and the yields of corresponding carbonates could also approach 100% (**3g, 3h**). Whereas the effect of secondary and tertiary alcohols on the reaction was undesirable (**3i, 3j**). It was found that the secondary alcohol isopropanol could react with CO_2 and propargylic alcohol, but the yield of desired product **3i** was only 28%. The tertiary alcohol tertiary butanol had little reaction activity for this reaction, After the reaction was proceeded for 6 h, the conversion of **1a** was 92%, but only an intermediate 4,4-dimethyl-5-methylene-[1,3]dioxolan-2-one (**M**) was formed, and the desired product **3j** was hardly detected.

Our experiments indicated that at shorter reaction time, an intermediate 4,4-dimethyl-5-methylene-[1,3]dioxolan-2-one (**M**, Scheme 2) of the reaction of CO_2, **1a** and **2a** could be detected by ^1H and ^{13}C NMR analysis.[23] Then we determined the time profiles of the reaction as shown in Figure 4. The substrate **1a** was completely converted in the first 4 h, while complete transformation of **M** with methanol needed a longer time. Therefore, we deduced that the synthesis of unsymmetrical organic carbonates from CO_2, propargylic alcohols and primary

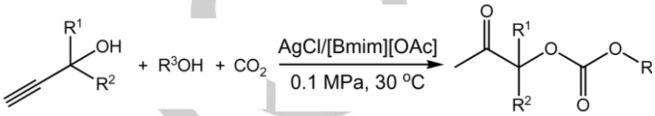
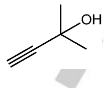
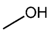
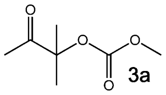
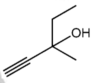
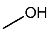
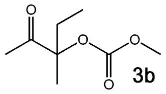
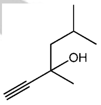
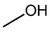
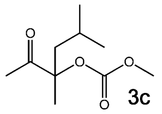
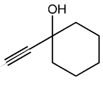
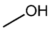
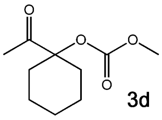
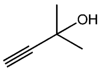
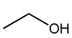
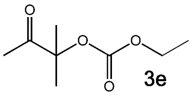
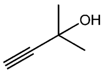
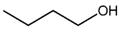
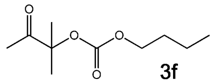
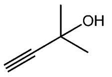
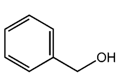
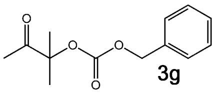
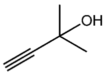
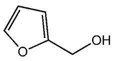
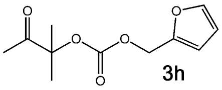
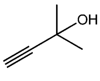
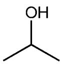
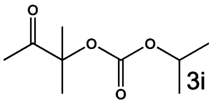
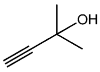
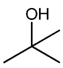
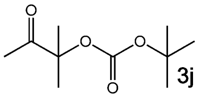


Table 2. Scope of the propargylic alcohols and primary alcohols substrates for the reaction.[a]

E	Propargylic alcohols	Primary alcohols	Product	t (h)	Y[b] (%)
1			 3a	6	>99 95[c]
2			 3b	6	>99 95[c]
3			 3c	10	>99 96[c]
4			 3d	14	>99 96[c]
5			 3e	14	>99 95[c]
6			 3f	18	>99 96[c]
7			 3g	14	>99 95[c]
8			 3h	14	>99 94[c]
9			 3i	6	28
10			 3j	6	< 1

[a] E=Entry. Reaction conditions: propargylic alcohol (1.5 mmol), primary alcohol (1.5 mmol), [Bmim][OAc] (1.5 mmol, 0.2974 g), AgCl (0.3 mmol, 0.0431 g), CO_2 (0.1 MPa), 30 ºC. [b] The yield was determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard. [c] Isolated yield.

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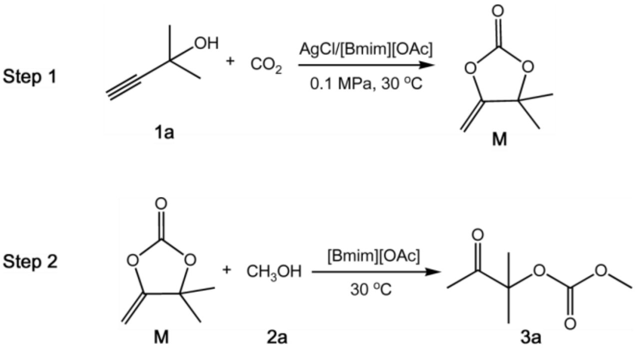
alcohols contained two steps, the cycloaddition of CO_2 with propargylic alcohols to form the α-alkylidene cyclic carbonates, and then the ring opening and tautomerization of cyclic carbonates, as shown in Scheme 2. Both primary alcohol andsecondary alcohol had activities for the step of the ring opening and tautomerization of cyclic carbonates (Table 2, entries 1 and 9), while the tertiary alcohol had little activity for this step (Table 2, entry 10). Therefore, as tertiary alcohols, the propargylic alcohols we used had high chemo-selectivity for this three-component reaction.



Scheme 2. The detail reaction route for the synthesis of unsymmetrical organic carbonates from CO_2 with propargylic alcohol and primary alcohol.

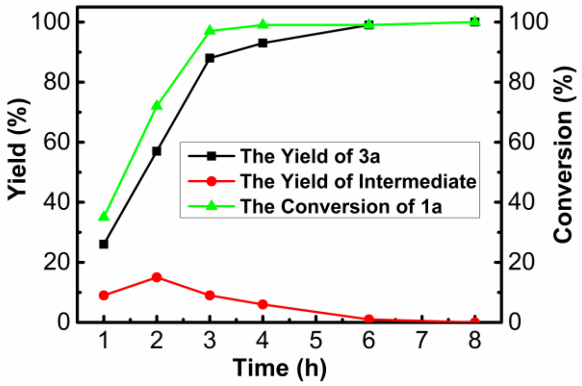


Figure 4. The time profiles of the conversion of **1a** and the yields of intermediate **M** and **3a**. Reaction conditions: **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0481 g), [Bmim][OAc] (1.5 mmol, 0.2974 g), AgCl (0.3 mmol, 0.0431 g), CO_2 (0.1 MPa), 30 °C and different reaction times; Yields were determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

As discussed above (Scheme 2), the reaction consisted of two steps: the cycloaddition of CO_2 with propargylic alcohols to form α-alkylidene cyclic carbonates (the first step) and the reaction of cyclic carbonate with primary alcohol (the second step). In order to clarify the roles of the components in AgCl/[Bmim][OAc] catalyst system, we studied their effects on each step of the reaction, and the results are given in Tables S1-S2. AgCl or [Bmim][OAc] had no catalytic activity for the synthesis of intermediate **M** (the first step) at room temperature (Table S1, entries 2-3). While AgCl/[Bmim][OAc] system could effectively accelerate the reaction with the yield of 70% in 3 h (Table S1, entry 4). The second step is the formation of **3a** via the ring opening and tautomerization of **M** and methanol. AgCl was not active for the reaction (Table S2, entry 2). IL [Bmim][Cl] was not active for the reaction either (Table S2, entry 3). However, IL [Bmim][OAc] itself could catalyze the reaction and **M** could be converted completely in 1 h (Table S2, entry 4). The results hint that the IL [Bmim][OAc], especially $[OAc]^-$, played an important role in promoting the second step.

The above results indicate that AgCl and [Bmim][OAc] accelerated the first step in Scheme 2 cooperatively. In addition, it is well known that the two substituted imidazolium cation, such as $[Bmim]^+$, can be changed into carbine after losing the proton,[24] but the three substituted imidazolium cation $[Bmmim]^+$ is stable and can rule out the possibility to form carbine. Table 1 showed clearly that the yield of target product promoted by AgCl/[Bmmim][OAc] system was 95% (Table 1, entry 15). Therefore, these results indicated that compared with $[OAc]^-$, imidazolium cation did not play the main role for the reaction. In addition, the results in Table 1 and Figure 1 all suggested the vital role of $[OAc]^-$. To study the role of $[OAc]^-$, the substrate **1a**, the mixture of **1a**/[Bmim][Cl] and **1a**/[Bmim][OAc] were examined by ^1H NMR spectroscopic analysis (Figure S1). It was found the ^1H signal of O-H in **1a** was a sharp single peak and appeared at δ=5.27 ppm (Figure S1, A). Because of the weak hydrogen bonding interaction by $[Cl]^-$ of [Bmim][Cl], the ^1H signal of O-H in **1a** in the mixture of **1a**/[Bmim][Cl] was shifted to 5.41 ppm while the peak form was never changed (Figure S1, B). However, the ^1H signal of O-H in **1a** was changed into a broad peak and shifted obviously when [Bmim][OAc] was added (Figure S1, C), which indicated that $[OAc]^-$ in [Bmim][OAc] could activate the alcoholic hydroxyl. On the basis of the experimental results of this work and the related knowledge in the literatures,[25-26] a possible mechanism for the catalytic reaction is proposed, which is shown in Figure 5. The $[OAc]^-$ of [Bmim][OAc] is a proton acceptor.[25] Thus, in the first step, with the proton hydrogen of the alcoholic hydroxyl activated by $[OAc]^-$, CO_2 electrophilic attack on the O atom of alkoxyl group becomes much easier. Thus, an acetic acid molecule and a carbonate anion can be formed. For the subsequent intramolecular cyclization process, the O atom in carbonate anion can attack the C atom in the C≡C bond because AgCl is an efficient catalyst for the activation of C≡C bond,[26] and transfer of the proton from acetic acid to the C≡C bond occurs simultaneously. As a result, the intermediate α-alkylidene cyclic carbonate is formed. Next, the target product can be formed by nucleophilic attack of the $[OAc]^-$ activated alcohol to the carbonyl of intermediate, with ring opening and tautomerization.

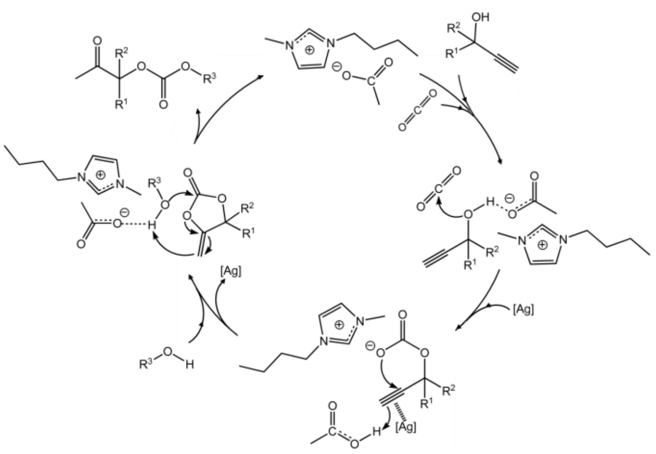


Figure 5. The possible mechanism for the reaction of atmospheric CO_2 with propargylic alcohols and primary alcohols.

Conclusions

In conclusion, using AgCl/[Bmim][OAc] as catalyst and solvent, a series of unsymmetrical organic carbonates can be synthesized efficiently by the reaction of CO_2 with propargylic alcohols and primary alcohols under ambient conditions. The yields of the desired products can approach 100%, and the catalyst system can be easily recovered and reused. The catalyst system not only combines the advantages of homogenous and heterogeneous catalysts, but also the easy separation of catalyst. We believe that this greener route has great potential application for producing unsymmetrical organic carbonates using CO_2 as a feedstock because of ambient reaction condition, very high yield, and efficient and reusable catalyst system.

Experimental Section

General procedure for the preparation of unsymmetrical organic carbonates: as an example, the procedure using **1a** and **2a** as the substrates are described, and those for other substrates are similar. In a typical experiment, **1a** (1.5 mmol, 0.1262 g), **2a** (1.5 mmol, 0.0484 g), [Bmim][OAc] (1.5 mmol, 0.2974 g) and AgCl (0.3 mmol, 0.0431 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO_2 into the reactor. Then the pressure of CO_2 was kept at 0.1 MPa using a balloon with CO_2. The reactor was placed in a water bath of 30 ºC and the reaction mixture was stirred for a desired time. After the reaction, the product was extracted by diethyl ether and the solvent was removed under vacuum to afford the desired carbonate **3a** as a colorless oil. After 5 times of recycle, the IL in the catalyst system was extracted by H_2O, and then was characterized by ^{1}H and ^{13}C NMR after removing H_2O under vacuum. The white precipitation that was insoluble in HNO_3 solution was AgCl.

The procedure for the preparation of the intermediate **M**. The procedures described in the literature were used.[23] In a sealable test-tube equipped with a magnetic stir bar was charged with ZnI_2 (0.3 mmol, 0.0958 g), 2-methyl-3-butyn-2-ol (1.5 mmo, 0.1262 g), triethylamine (1.5 mmol, 0.1518 g). The reaction vessel was sealed and the pressure of CO_2 was kept at 1 MPa. The test-tube was placed in a water bath of 30 ºC and was allowed to stir overnight. After the reaction, the reactor was placed in ice water for 20 minutes and CO_2 was vented slowly. Then dichloromethane (5 mL) was added in the reaction mixture. After removing precipitate by centrifuging, the reaction mixture was washed with water, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum to afford **M** as a colorless oil.

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Keywords: CO_2 Fixation • Ionic Liquid • Ambient Conditions • Unsymmetrical Organic Carbonates

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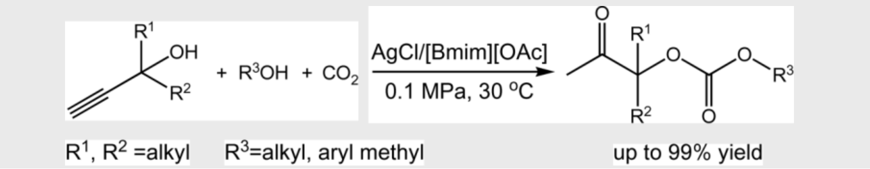

A series of unsymmetrical organic carbonates can be synthesized efficiently by the reaction of CO_2 with propargylic alcohols and primary alcohols under ambient conditions using AgCl/[Bmim][OAc] as catalyst and solvent, and the yields of the desired products can approach 100%.

Jiayin Hu[1,2], Jun Ma[1], Lu Lu[1,2], Qingli Qian[1], Zhaofu Zhang[1], Chao Xie[1,2], Buxing Han[1,2]**

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Synthesis of Unsymmetrical Organic Carbonates using CO_2 as a Feedstock in AgCl/Ionic Liquid System at Ambient Conditions