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Tetrabutylphosphonium-Based Ionic Liquid Catalyzed CO_2 Transformation at Ambient Conditions: A Case of Synthesis of α-Alkylidene Cyclic Carbonates

Yunyan Wu,[‡a,b] Yanfei Zhao,[‡a] Ruipeng Li,[a] Bo Yu,[a] Yu Chen,[a,b] Xinwei Liu,[a,b] Cailing Wu,[a,b] Xiaoying Luo,[a,b] and Zhimin Liu[*a, b]

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

KEYWORDS: Tetrabutylphosphonium-based ionic liquids, multiple-site, CO2 transformation, ambient conditions, α-alkylidene cyclic carbonates

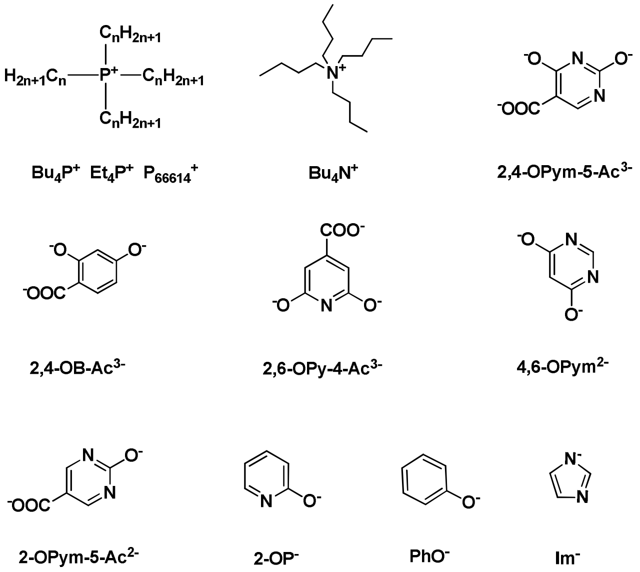
ABSTRACT: A series of tetrabutylphosphonium ($[Bu_4P]^+$)-based ionic liquids (ILs) with multiple-site for CO_2 capture and activation in their anions are reported, which could efficiently catalyze the cyclization reaction of propargylic alcohols with CO_2 at ambient conditions. Especially, the IL, $[Bu_4P]_3$[2,4-OPym-5-Ac], which has three interaction sites for attracting CO_2 together with a pK_{a1} value of 9.13, exhibited the best performance, affording a series of α-alkylidene cyclic carbonates in moderate to good yields. The mechanism exploration demonstrated that IL served as a bifunctional catalyst with anion simultaneously activating CO_2 via multiple-site cooperative interactions and the C≡C triple bond in propargylic alcohol via inductive effect, thus resulting in the production of α-alkylidene cyclic carbonates.

As an abundant, nontoxic and renewable C1 building block, the transformation of CO_2 into value-added chemicals and fuels such as methanol,[1] formic acid,[2] cyclic carbonates[3] and others[4] is both environmentally and practically attractive, and has been widely investigated. However, CO_2 is a thermodynamically stable molecule, thus its transformation under mild conditions, especially at metal-free and ambient conditions is challenging. To date, many efforts have been dedicated to the transformation of CO_2 under mild conditions with focus on developing efficient catalysts.[3,5] For example, metal-free catalysts including ionic liquids,[5d-5f] N-heterocyclic carbenes[5g-5h] and frustrated Lewis pairs[5i-5j] have been presented to be very effective for the CO_2 conversion. Although some progress has been made, well designed catalytic system that is capable of activating CO_2 and further catalysing its transformation at metal-free and ambient conditions is still highly desirable.

Ionic liquids (ILs), composed entirely of cations and anions, can be engineered specifically via the careful design and selection of novel component ions, which therefore have displayed promising applications in many areas, especially in catalysis and gas absorption.[6] To date, a series of CO_2-reactive site-containing ILs, including azolate-,[7] phenolate-,[8] amino acid-containing anion-[9] and pyridine-containing anion-based ILs,[10] have been presented as efficient CO_2 adsorbent via forming carbamates and/or carbonates. These ILs could activate CO_2 via cooperative effects from their cation and anion, thus further resulting in the chemical transformation of CO_2 under mild reaction conditions. For example, the protic IL, [DBU][TFE], that could capture equimolar CO_2, was proved to be capable of catalyzing CO_2 transformation under ambient conditions in the synthesis of quinazo-line-2,4(1H,3H)-dione from CO_2 and 2-aminobenzonitriles.[11] Multiple-site ILs, $[P_{4444}]$[2-OP], possessing two kinds of interacting site with CO_2, were demonstrated to be efficient for catalysing the cycloaddition reactions of atmospheric CO_2 with epoxides at room temperature under metal- and halogen-free conditions.[12]

α-Alkylidene cyclic carbonates are an important class of heterocyclic frameworks in natural products with potential bioactivities and also versatile intermediates in organic synthesis and polymer chemistry.[13] The atom-economic reaction between propargylic alcohols and CO_2 is an attractive route to α-alkylidene cyclic carbonates. Various metal catalysts, including, $[(n\text{-}C_4H_9)_4N]_2WO_4$,[14] ZnI_2/Et_3N,[15] AgOAc/DBU,[16] $AgOAc/(n\text{-}C_7H_{15})_4NBr$,[17] Ag_2WO_4/Ph_3P,[18] $[(PPh_3)_2Ag]_2CO_3$,[19] AgOAc/$[P_{66614}]$[DEIm],[20] AgNPs/SMR[21] have been proved to be efficient for this reaction at low temperature and pressure. Recently, organo-based metal-free catalysts, including N-heterocyclic carbenes (NHCs),[22] alkoxide-functionalized imidazolium betaine,[23] phosphorus ylide (P-ylide) CO_2 adducts[24] and ILs[25] have emerged as powerful catalysts, which realized the reaction under mild reaction conditions. However, only Ag-based catalysts have realized this transformation at room temperature and atmospheric pressure.[19,21]

In this work, we report a series of tetrabutylphosphonium ($[Bu_4P]^+$)-based ILs with multiple-site for CO_2 capture and activation in their anions as shown in Scheme 1, which could efficiently catalyze the cyclization reaction of propargylic alcohols with CO_2 under ambient conditions. Especially, the IL, $[Bu_4P]_3$[2,4-OPym-5-Ac], which has three interaction sites to attract CO_2 together with a pK_{a1} value of 9.13, was found to be very efficient for this kind of reaction, affording a series of α-alkylidene cyclic carbonates in moderate to good yields. The mechanism exploration demonstrated that the cooperative interaction from multiple-interaction sites in the IL anion simultaneously activated CO_2 and the C≡C triple bond in propargylic alcohols, thus resulting in the production of α-alkylidene cyclic carbonates.



Scheme 1. The anion and cation structures in as-designed multiple active-site ILs and ILs for control experiment.

The $[Bu_4P]^+$-based ILs with different interaction sites in anions as shown in Scheme 1 were synthesized via deprotonation of weak proton donors, including 2,4-dihydroxypyrimidine-5-carboxylic acid (2,4-OPym-5-Ac), 2,4-dihydroxybenzoic acid (2,4-OB-Ac), 2,6-dihydroxypyridine-4-carboxylic acid (2,6-OPy-4-Ac), 4,6-dihydroxypyrimidine(4,6-OPym), 2-hydroxypyrimidine-5-carboxylic acid (2-OPym-5-Ac), 2-hydroxypyridine (2-OP), phenol (PhO) and imidazole (Im), with tetrabutylphosphonium hydroxide ($[Bu_4P][OH]$) (see Supporting Information). Most of these ILs were in the liquid states at room temperature. NMR analysis confirmed their formation (Figure S1-S11), and TG analysis showed that they are thermally stable from 445 K to 511 K (Figure S12-16). The resultant ILs could efficiently capture CO_2 at room temperature and atmospheric pressure, confirmed by the NMR analysis (Figure S17-S24). Depended on the interaction sites in their anions, these ILs showed different ability to capture CO_2. For example, $[Bu_4P]_3$[2,4-OPym-5-Ac] could attract CO_2 molecules via three interaction sites in the anion, and the uptake of CO_2 could reach up to 1.46 mol per molar IL at ambient conditions. As shown in the ^{13}C NMR spectrum of the IL exposed to CO_2 at ambient conditions (Figure 1 and S17), two new signals appeared at δ = 165.9, 158.5 ppm, which were attributed to the carbonyl carbon atoms of carbonates from the multiple O electronegative sites in anion and CO_2. This suggests that this IL could efficiently capture CO_2 chemically, which may result in the activation of CO_2. IR and ^{31}P NMR analysis were also performed to identify the as-formed poly-carbonates. A new band around 1603 cm^{-1} appeared in each IR spectrum of the IL exposed to CO_2 for desired time (Figure S25), which was ascribed to the asymmetrical stretching vibration of carboxylate ion in O-CO_2 interaction, suggesting the formation of poly-carbonates from the IL and CO_2. Moreover, the band became more intense as prolonging the absorption time, indicating that the CO_2 uptakes by the IL increased with the time. Both signals in ^{31}P NMR spectrum showed slight shifts after the IL exposed to CO_2 (Figure S26), probably resulting from the influence of the formation of poly-carbonates in anion.

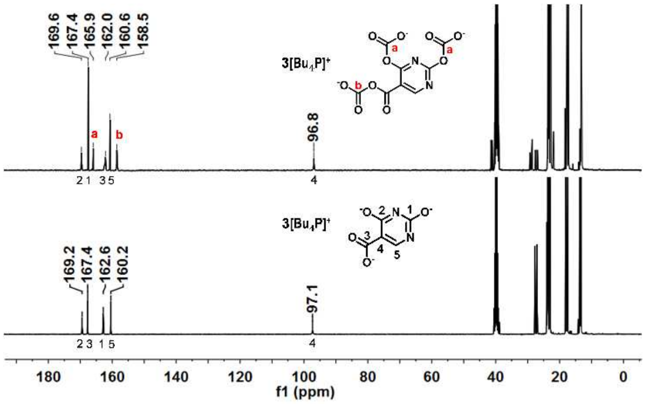


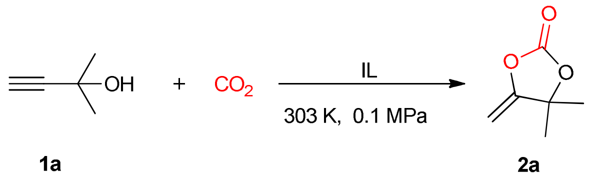
Figure 1. ^{13}C NMR spectrum of pure $[Bu_4P]_3$[2,4-OPym-5-Ac] and the as-formed intermediate following the exposure of $[Bu_4P]_3$[2,4-OPym-5-Ac] to CO_2 (0.1 MPa; $[D_6]$-DMSO, 0.6 mL, 298 K).

All the resultant ILs were examined for catalyzing the reaction of 2-methyl-3-butyn-2-ol (1a) with CO_2, and the results are shown in Table 1. It was indicated that the $[Bu_4P]^+$-based ILs with interaction sites in anions for CO_2 capture were effective for catalysing this reaction under ambient conditions, showing different activities depending on their chemical structures. $[Bu_4P]_3$[2,4-OPym-5-Ac] showed the best performance, producing α-alkylidene cyclic carbonate 2a in 79% yield within 20 h at room temperature and atmospheric pressure (Table 1, entry 1), and increasing CO_2 pressure to 2 MPa resulted in enhanced product yield up to 91% within shorter time of 5 h (Table 1, entry 2). The IL maintained its original structure after the reaction, confirmed by ^{1}H NMR analysis (Figure S27). In contrast, the other two ILs, $[Bu_4P]_3$[2,4-OB-Ac] with three interaction sites and $[Bu_4P]_3$[2,6-OPy-4-Ac] with four interaction sites in their anions, displayed lower activity for this reaction though they also could efficiently attract CO_2 with high capacity (Table 1, entries 3 and 4). This implies that the interaction between the IL and CO_2 was not the only one factor to influence the activity of the ILs.

Though the ILs having two or one reactive sites in their anions were also effective for the reaction, they showed lower activity (Table 1, entries 5-9), suggesting that the interaction sites to bind CO_2 in the anion considerably influenced the activity of the ILs. The reaction did not occur in the presence of $[Bu_4P]$[Br] (Table 1, entry 10), probably because this IL could not capture CO_2. This indicates that the capture and activation of CO_2 by the IL via the interaction site in the anion was crucial to the reaction. From the above results, it also can be observed that the ILs with the same interaction sites in their anions showed different activities, implying that the inherent properties of the ILs played the key role in catalysing the reaction.

Given that the resultant ILs are basic, the pK_{a1} values of the anions in tert-butyl alcohol (*t*-BuOH) were computed by density functional theory (DFT) calculation[6c,20] and listed in Table 1. In the view of the relationship between the product yield and pK_{a1} value of IL anion, we postulated that the proper basicity also plays an important role in the catalytic reaction process. For the ILs with three interaction sites in their anions, $[Bu_4P]_3$[2,4-OPym-5-Ac] with a pK_{a1} value of 9.13 showed the highest product yield (79%; Table 1, entry 1), while $[Bu_4P]_3$[2,4-OB-Ac] with a pK_{a1} value of 9.97 gave a slightly lower yield of 66 % (Table 1, entry 3). Notably, $[Bu_4P]_3$[2,6-OPy-4-Ac] with a pK_{a1} value of 5.45 gave a very low yield of 15% (Table 1, entry 4), although it could attract CO_2 with an uptake of 3.26 mol per molar IL. These results indicate that the basicity of the ILs was an important factor to influence the catalytic activity of the ILs. The IL with strong basicity led to side reactions, while the IL with weak basicity exhibited poor catalytic activity. Therefore, the ILs with higher or lower pK_{a1} values showed poor performances, and only the ILs with appropriate pK_{a1} value displayed the high efficiency. The similar phenomenon was also observed in the base/AgOAc catalytic system.[20] From the above findings, it can be deduced that increasing electronegative sites with proper pKa value of anion is a facile way to improve fixation and transformation of CO_2. The regularity in pKa value found here may provide an instruction to design basic ILs for alkaline-catalyzed reactions. In addition, $[Bu_4N]_3$[2,4-OPym-5-Ac], with the same anion as $[Bu_4P]_3$[2,4-OPym-5-Ac], gave inferior product yield (Table 1, entry 11), implying the IL cation also played an important role in this reaction. In comparation with $[Bu_4P]_3$[2,4-OPym-5-Ac], $[Et_4P]_3$[2,4-OPym-5-Ac] and $[P_{66614}]_3$[2,4-OPym-5-Ac] afforded lower product yields (Table 1, entries 1, 12 and 13), following the order: $[P_{66614}]_3$[2,4-OPym-5-Ac] (8%) < $[Et_4P]_3$[2,4-OPym-5-Ac] (20%) < $[Bu_4P]_3$[2,4-OPym-5-Ac] (79%). These results indicate that the catalytic activities of these ILs were significantly affected by the carbon chains of the IL cation, and C_4 chain was found to be the best.

Table 1. Reaction of 2-methyl-3-butyn-2-ol with CO_2 catalyzed by different IL catalysts.[a]

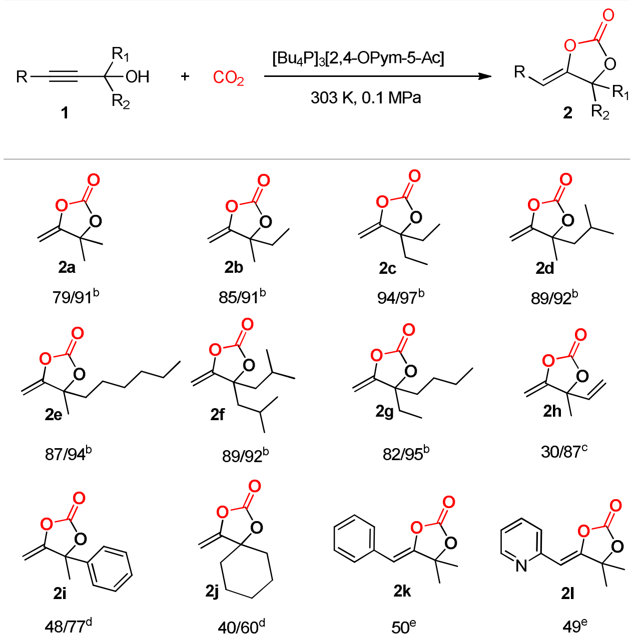


Entry	Catalysts	pK_{a1}	Yield %[b]
1	$[Bu_4P]_3$[2,4-OPym-5-Ac]	9.13	79
2	$[Bu_4P]_3$[2,4-OPym-5-Ac]	9.13	91
3	$[Bu_4P]_3$[2,4-OB-Ac]	9.97	66
4	$[Bu_4P]_3$[2,6-OPy-4-Ac]	5.45	15
5	$[Bu_4P]_2$[4,6-OPym]	8.49	69
6	$[Bu_4P]_2$[2-OPym-5-Ac]	5.45	33
7	$[Bu_4P]$[2-OP]	12.32	40
8	$[Bu_4P]$[PhO]	16.19	27
9	$[Bu_4P]$[Im]	18.30	10
10	$[Bu_4P]$[Br]	-	0
11	$[Bu_4N]_3$[2,4-OPym-5-Ac]	-	13
12	$[Et_4P]$[2,4-OPym-5-Ac]	-	20
13	$[P_{66614}]$[2,4-OPym-5-Ac]	-	8

[a] Reaction conditions: 2-methyl-3-butyn-2-ol (2 mmol), catalyst (0.2 mmol), CO2 (0.1 MPa), 303 K, 20 h; [b] Yields were determined by ^{1}H NMR spectroscopy using N,N-dimethylformamide as an internal standard; [c] 2MPa, 5h.

Based on the above results, $[Bu_4P]_3$[2,4-OPym-5-Ac] was applied to various terminal propargylic alcohols reacting with CO_2 at ambient conditions, and the results are listed in Table 2. It was indicated that this IL allowed all the reactions to proceed smoothly, affording the corresponding α-alkylidene cyclic carbonates (2a-2g) in good to excellent yields under the experimental conditions. Especially, excellent yields could be achieved even within short reaction time (e.g., 5h) at 2 MPa. Notably, propargylic alcohols with bulky isobutyl groups reacted rapidly with high product yields in the presence of this IL catalyst (2d and 2f). The better performance of $[Bu_4P]_3$[2,4-OPym-5-Ac] for the substrates with big steric hindrance may be ascribed to the unique interaction way of the anion of the IL with the reactants in the reaction process. In contrast, propargylic alcohols with electron-withdrawing groups (vinyl) exhibited inferior reactivity especially under ambient conditions (2h), whereas relatively high CO_2 pressure (e.g., 3 MPa) resulted in improved product yields. Propargylic alcohols with cyclohexyl and phenyl substituents showed lower activity (2i and 2j), probably due to the steric hindrance and ring strain. Also, $[Bu_4P]_3$[2,4-OPym-5-Ac] worked well to the substrates with a phenyl group or pyridyl group at the terminal position (2k and 2l). All the above results demonstrate that $[Bu_4P]_3$[2,4-OPym-5-Ac] was an efficient metal-free catalyst for propargylic alcohols with CO_2 to produce α-alkylidene cyclic carbonates at ambient conditions.

Table 2. Synthesis of various α-alkylidene cyclic carbonates.[a]



[a] Reaction conditions: Substrate (2 mmol), catalyst (0.2 mmol), CO2 (0.1 MPa), 303 K, 20 h, Yields were determined by ^{1}H NMR spectroscopy using N,N-dimethylformamide as an internal standard; [b] CO2 (2 MPa), 5h; [c] CO2 (3 MPa), 20 h; [d] CO2 (2 MPa), 20 h; [e] catalyst (0.4 mmol), CH3CN (2 mL), 20h.

To explore the reaction mechanism, the interactions between $[Bu_4P]_3$[2,4-OPym-5-Ac] and CO_2 or **1a** were examined by NMR and FTIR analysis. As stated in the CO_2 adsorption experiment by the IL, CO_2 was captured by the anion $[2,4\text{-OPym-5-Ac}]^{3-}$ to form poly-carbonates, which was also detected when the CO_2 absorption was carried out in *t*-BuOH solution of the IL (Figure S28). These results suggest that the poly-carbonates from the IL and CO_2 may be key intermediates in the reaction process of propargylic alcohols with CO_2. To confirm this, **1a** was mixed with this poly-carbonates at room temperature, and **2a** was detected after 5h accompanied with the disappearance of poly-carbonates confirmed by the ^{13}C NMR analysis (Figure S29), thus suggesting that poly-carbonates were indeed the key intermediate in the formation of the final product. In the ^{1}H NMR spectrum of the mixture of $[Bu_4P]_3$[2,4-OPym-5-Ac] and **1a**, the ^{1}H signal of O-H in **1a** broadened obviously and shifted from 5.30 to 5.82 ppm (Figure S30), indicating the hydrogen-bonding interaction between the anion of IL and OH. In the ^{13}C NMR spectrum of the IL and **1a** mixture (Figure 2, S31, S32), the terminal carbon signal of the triple bond in **1a** shifted upfield from 70.3 ppm to 68.9 ppm and the internal carbon signal showed a downfield shift from 88.6 ppm to 89.4 ppm. In the FTIR spectrum of the mixture, the band assigned to the alkyne -C≡C- stretching vibration showed a shift from 2118 cm^{-1} to 2108 cm^{-1} (Figure S33). However, no obvious changes were observed in the corresponding ^{31}P NMR spectrum (Figure S34). From the these findings, it can be deduced that the anion of the IL activated the -C≡C- in **1a**. It is reasonable that the O-H bond in **1a** was activated by the anion [2,4-OPym-5-Ac] via hydrogen bonding, resulting in the electron redistribution of alkynyl carbon, thus indirectly activating the triple bond via inductive effect, which may facilitate the poly-carbonate intermediate to nucleophilic addition on the triple bond. The above results indicate the anion of IL played a key role in activating CO2 and substrates (e.g., **1a**) in the reaction process.

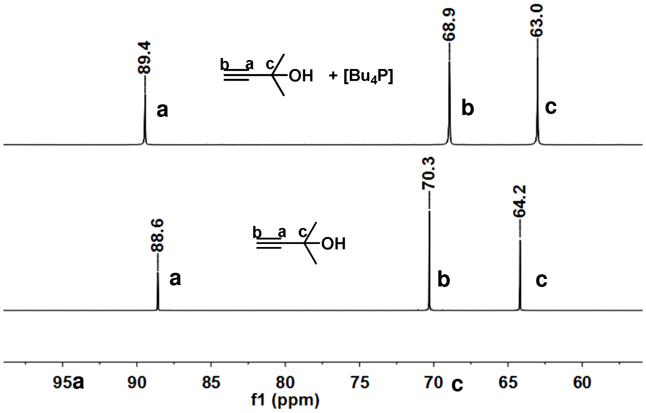
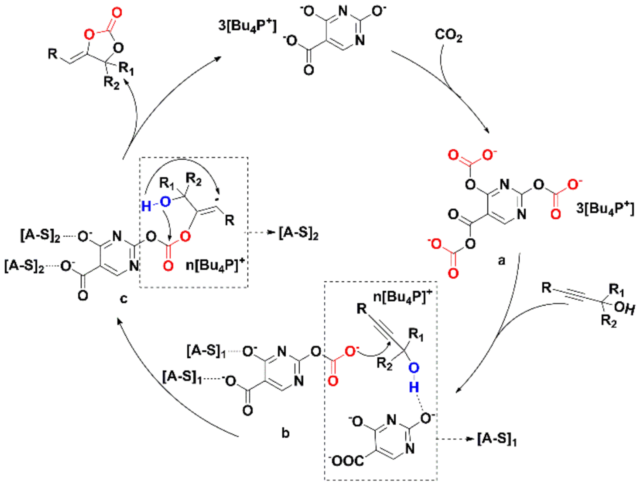


Figure 2. ^{13}**C NMR spectrum of pure 2-methyl-3-butyn-2-ol and the mixture of** $[Bu_4P]_3$**[2,4-OPym-5-Ac] and** $[Bu_4N]_3$**[2,4-OPym-5-Ac] (0.1 mmol) and 2-methyl-3-**

butyn-2-ol (10 mmol) (298 K, [D_6]-DMSO in capillary as an internal standard).



Scheme 2. Possible reaction pathway

On the basis of the experimental results and previous reports,[15-25] a possible machanism was proposed, as shown in Scheme 2. In the presence of IL, CO_2 is captured and activated by the anion of IL to form poly-carbonate intermediate **a**, meanwhile the O-H bond in propargylic alcohol is activated by the anion [2,4-OPym-5-Ac]$^{3-}$ via hydrogen bonding, thus further activating the triple bond in propargylic alcohol via inductive effect. Then, the intermediate **a** adds to the triple bond of propargylic alcohol via nucleophilic attack, forming intermediate **b**, followed by hydrogen migration from the hydroxy group of the alcohol to produce intermediate **c**. Finally, the alkoxide anion of intermediate **c** attacks the carbonyl carbon atom to form the α-alkylidene cyclic carbonate, with the release of the IL.

In summary, a series of [Bu_4P]$^+$-based ILs with multiple-site for CO_2 capture and activation in their anions were presented, which could efficiently catalyze the cyclization reaction of propargylic alcohols with CO_2 at ambient conditions. The IL, [Bu_4P]$_3$[2,4-OPym-5-Ac], which has three interaction sites for attracting CO_2 together with a pK_{a1} value of 9.13, exhibited highly efficient efficiency, affording a series of α-alkylidene cyclic carbonates in moderate to good yields. The mechanism exploration demonstrated that the IL served as a bifunctional catalyst with anion simultaneously activating CO_2 via multiple-site cooperative interactions and the C≡C triple bond in propargylic alcohol substrate via inductive effect, thus resulting in the production of α-alkylidene cyclic carbonates. This kind of ILs may find promising applications in CO_2 transformation under mild conditions.

ASSOCIATED CONTENT

Supporting Information. General experimental methods, yields determination and characterization of the products. "This material is available free of charge via the Internet at http://pubs.acs.org."

AUTHOR INFORMATION

Corresponding Author

*E-mail: liuzm@iccas.ac.cn

Author Contributions

‡These authors contributed equally.

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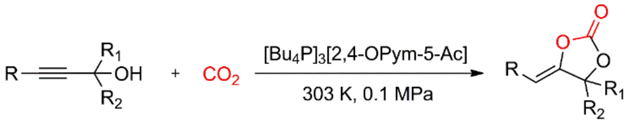

green, metal-free

up tp 94% yield