Green Chemistry

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C4GC02033B

Journal Name

RSCPublishing

ARTICLE

A Route to Convert CO_2: Synthesis of 3,4,5-Trisubstituted Oxazolones

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Production of value-added chemicals using carbon dioxide (CO_2) as a feedstock is favorable to the sustainable development of chemical industry. In this work, we discovered for the first time that CO_2 could react with propargylic amines to produce 3,4,5-trisubstituted oxazolones, a class of very useful chemicals. It was found that ionic liquid (IL) 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) could catalyze the reactions efficiently under atmospheric pressure at metal-free condition. It was also found that [Bmim][OAc] and IL 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([Bmim][Tf_2N]) had excellent synergistic effect for promoting the reactions. The [Bmim][OAc]/[Bmim][Tf_2N] catalytic system could be reused at least five times without loss in catalytic activity and selectivity. The reaction mechanism was proposed on the basis of density functional theory (DFT) calculation and the experimental results.

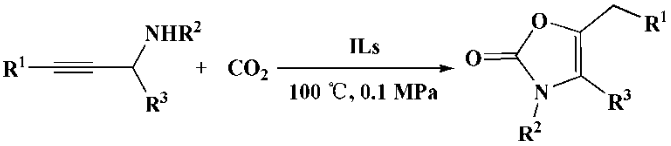
Introduction

Carbon dioxide (CO_2) is the major greenhouse gas. It is also an abundant, nontoxic, non-flammable, easily available, and renewable carbon source.[1-4] Transformation of CO_2 to useful products, such as cyclic carbonates,[5-8] urea derivatives,[9] methanol,[10-12] formic acid,[13-15] methyl formate,[16-17] carboxylic acids,[18-19] N-methylated products,[20-21] and polymers[22] *etc.*, is of great importance from both scientific and practical viewpoints. Although much effort has been made to convert CO_2, the variety of reactions is very limited because CO_2 is thermodynamically stable and kinetically inert.[23] Exploration of new reactions for the transformation of CO_2 into value-added chemicals is a long-term interesting topic. The chemical fixation of CO_2 through the cyclization of propargylic amines with CO_2 to provide 2-oxazolidinones has been found to proceed with various catalysts such as organometallic complexes of palladium or gold, silver salts and organic strong bases.[24-27] Recently, Yamada and co-worker showed the excellent Ag/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) catalyst which can provide 2-oxazolidinones or tetramic acid through the reaction of CO_2 and propargylic amines.[28-29] However, the synthesis of oxazolones and their derivatives with CO_2 and propargylic amines has not been reported.

Oxazolones and their derivatives are very useful compounds in different fields. They have been successfully used as versatile starting materials for various organic reactions.[30-33] Oxazolones also have important biological activities such as excellent cardiotonic activity,[34] anti-HIV activity,[35] and are potent and selective cyclooxygenase-2 inhibitors.[36] Moreover, oxazolones exhibit promising photochemical and photophysical activities,[37-38] and can be used in semiconductor devices such as electrophotographic photoreceptors and non-linear optical materials.[39-40] Some protocols have been developed for the synthesis of polysubstituted oxazolones,[41] especially for the 3,4,5-trisubstituted oxazolones. It was reported that refluxing of 3-nosyloxy-2-ketoesters with methyl carbamate and tosic acid (TSA) in toluene could afford oxazolones.[42] Catalyzed by rhodium octanoate and base, diazocarbonyls and phenylcarbamate could also be transformed into oxazolones.[43] Acyl chlorides or α-diketone was also used as the starting materials for the synthesis of oxazolones via several steps.[44-45] Oxazolones were synthesized by the cyclization of propargylic alcohols with n-butylamine and high pressure CO_2 using CuI as the catalyst.[46] Recently, some 3,4,5-trisubstituted oxazolones were prepared by the reaction of N-alkynyltert-butyloxycarbamates and aromatic halides using organometal complexes as the catalysts.[47] Clearly, exploration of efficient, simple, cheap, and green routes to synthesize 3,4,5-trisubstituted oxazolones is highly desirable.

It is well known that ionic liquids (ILs) with low melting point (e.g. below 100 °C) have some unusual properties, such as negligible vapor pressure, excellent solvents for both organic and inorganic substances, and their functions can be designed by changing their structures and functional groups.[48-51] In recent years, applications of ILs in different fields have attracted considerable attention. Especially, ILs have shown great potential in chemical reactions as solvents and catalysts.[52]

Herein, we discovered for the first time that atmosphere CO_2 could react with propargylic amines to generate 3,4,5-trisubstituted oxazolones without any metal catalyst (Scheme 1). For these new reactions, simple and reusable IL 1-butyl-3-methylimidazolium acetate/1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([Bmim][OAc]/[Bmim][Tf_2N]) system was found to be very effective catalyst and solvent at atmospheric CO_2 pressure. The mechanism of the reactions was proposed by combination of experimental technique and quantum chemistry calculation.



Scheme 1 The reaction of CO_2 and propargylic amines to synthesize 3,4,5-trisubstituted oxazolones.

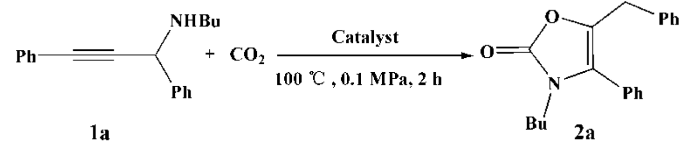
Results and Discussion

Screening and reusability of the catalyst system

Firstly, various catalysts including inorganic base Cs_2CO_3, organic bases DBU, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and IL ([Bmim][OAc]) were tested using propargylic amine (**1a**) as substrate and N,N-dimethylformamide (DMF) as solvent at 100 °C and 0.1 MPa CO_2 within 2 h, and the results are given in Table S1. The results showed that the reaction did not occur in the absence of catalyst. The yield of target product 5-Benzyl-3-butyl-4-phenyl-3H-oxazol-2-one (**2a**) with IL [Bmim][OAc] was significantly higher than that with the organic or inorganic bases. Then, the catalytic performances of various ILs were tested using the reaction of CO_2 with **1a** at atmospheric pressure, and the results are presented in Table 1. The reaction did not occur in the absence of IL (entry 1). The ILs 1-butyl-3-methylimidazolium perchlorate ([Bmim][ClO_4]), [Bmim][Tf_2N], 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), and 1-butyl-3-methylimidazolium thiocyanate ([Bmim][SCN]) had no catalytic activity for the reaction (entries 2-5). Interestingly, the basic ILs showed catalytic activity (entries 6-11). Among them, the ILs with acetic acid anion ($[OAc]^-$) had high activity with >99% conversion of **1a** (entries 8-11). [Bmim][OAc] showed best activity for the reaction, and the yield of **2a** was 73% as **1a** was converted completely (entry 11). We tried to improve the yield of **2a** by changing the amount of [Bmim][OAc] and reaction temperature, but the maximum selectivity was 73% (Figure S1) and the main by-product determined by GC/MC was chalcone (Scheme S1).

The effects of various solvents on the yield of **2a** were studied using [Bmim][OAc] as the catalyst, and the results are given in Table 2. When DMF, dimethyl sulfoxide (DMSO), and toluene were used as the solvents, the yields of **2a** were 67%, 70%, and 72%, respectively (entries 1-3, Table 2), which were similar to that in neat [Bmim][OAc] (73%, entry 11, Table 1). Interestingly, when ILs [Bmim][ClO_4], 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][CF_3SO_3]), and [Bmim][Tf_2N] were used as the solvents, the yields of **2a** were considerably higher. Especially, the yield could reach 88% as [Bmim][Tf_2N] was used as the solvent, indicating that [Bmim][OAc] and [Bmim][Tf_2N] had a synergistic effect for enhancing the selectivity of **2a** effectively. Thus, the IL mixture [Bmim][OAc]/[Bmim][Tf_2N] was utilized as the catalytic system to study the effects of temperature and the amounts of the ILs on the reaction at atmospheric pressure of CO_2 (Figure S2), and confirmed the optimal reaction conditions (entry 6, Table 2).

Table 1 Reaction of CO_2 with propargylic amine **1a** in various ILs.[a]



Entry	Catalysts	C^b/%	Y^b/%	S/%
1	--	0	0	--
2	[Bmim][ClO_4]	0	0	--
3	[Bmim][Tf_2N]	0	0	--
4	[Bmim][BF_4]	0	0	--
5	[Bmim][SCN]	0	0	--
6	[Bmim][CF_3OAc]	5	0	0
7	[Bmim][$(EtO)_2PO_2$]	26	8	30
8	[DBUH][OAc]	>99	40	40
9	[Emim][OAc]	>99	61	61
10	[Omim][OAc]	>99	67	67
11	[Bmim][OAc]	>99	73	73

[a] C = Conversion, Y = Yield, S = Selectivity. Typical reaction conditions were as follows until otherwise stated: 0.5 mmol of **1a**, 0.5 mmol of IL, 0.1 MPa CO_2, 100 °C, 2 h. [b] Conversion and yield were determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

Table 2 Reaction of **1a** with CO_2 in various solvents catalyzed by [Bmim][OAc].[a]

Entry	Solvent	C^b/%	Y^b/%	S/%
1	DMF	>99	67	67
2	DMSO	>99	70	70
3	Toluene	>99	72	72
4	[Bmim][CF_3SO_3]	>99	83	83
5	[Bmim][ClO_4]	>99	84	84
6	[Bmim][Tf_2N]	>99	88	88

[a] C = Conversion, Y = Yield, S = Selectivity. Typical reaction conditions were as follows until otherwise stated: 0.5 mmol of **1a**, 0.5 mmol solvent, 0.25 mmol of [Bmim][OAc], 0.1 MPa CO_2, 100 °C, 12 h. [b] Conversion and yield were determined by ^1H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

The reusability of the IL mixture [Bmim][OAc]/[Bmim][Tf_2N] was tested under the optimal reaction conditions. The results are given in Figure S3. The

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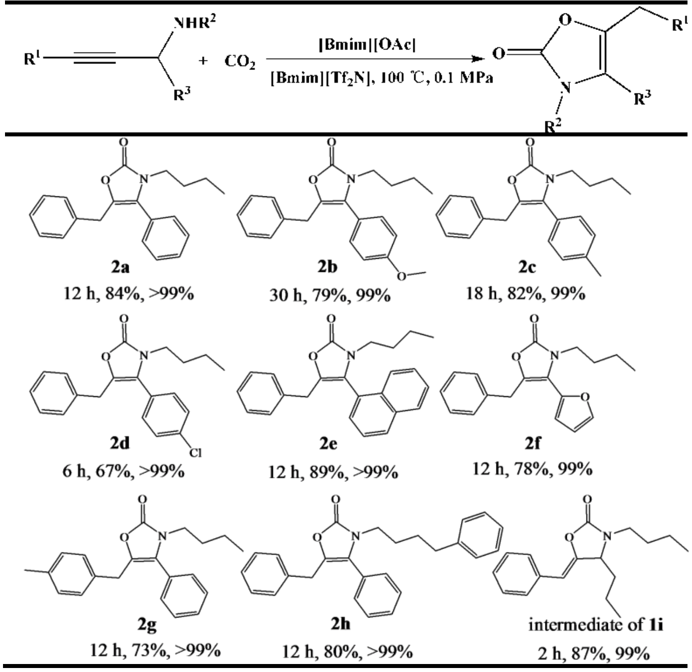
catalytic activity and selectivity of the ILs were not changed after reused five times. The structures of the ILs recycled after five times were detected by ^{1}H NMR and ^{13}C NMR spectra, and the results given in Supporting Information indicated that the ILs maintained the same structures as the virgin ones.

Versatility of the catalyst system

The reactions of CO_2 with a range of different substituted propargylic amines were then conducted under the optimized reaction conditions. The reaction times, isolated yields and the conversions are summarized in Table 3. In general, the reactivity of the propargylic amines depended strongly on the electronic properties of R^3 (**1a**-**1d**). When R^3 was a relatively electron-rich aromatic substituent (**1b** and **1c**), a longer time was required than that when R^3 was phenyl substituent (**1a**). However, when R^3 was an electron-poor 4-chloropnenyl substituent (**1d**), a shorter time was needed to complete the conversion of the propargylic amine. The reactivity of the propargylic amines follows the order of **1d**>**1a**>**1c**>**1b**. Another point was the effect of the conjugation of R^3 on the reactivity of the propargylic amines. It can be seen from Table 3 that the propargylic amines with a highly conjugative R^3 (**1e**) generated high yield of the desired product. But, for **1i** with an aliphatic R^3, the intermediate was obtained within 2 hours instead of the target product **2i**, and with the increasing of time, desired product **2i** was not detectable. The propargylic amines with different substituted groups R^1 and R^2 were also studied (**1g** and **1h**), and good yields of the corresponding 3,4,5-trisubstituted oxazolones (**2g** and **2h**) were obtained. The above results confirmed the versatility of the new methodology for producing 3,4,5-trisubstituted oxazolones.

Table 3 The isolated yields of the products for the reactions using different propargylic amines at the optimal reaction conditions.



Possible mechanism

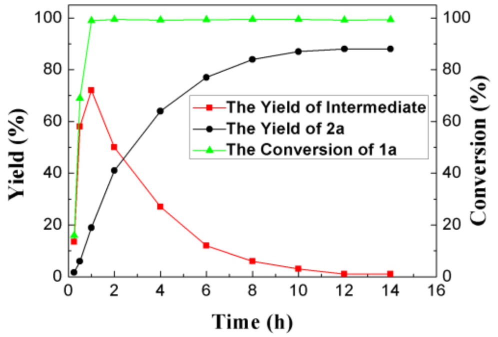
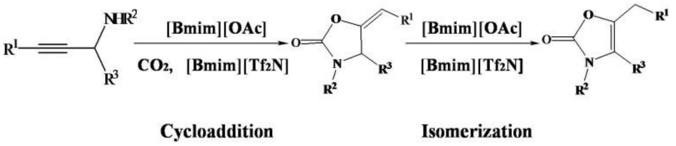
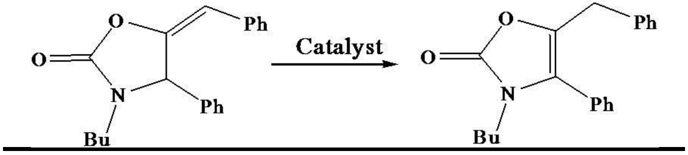


Fig. 1 The time profiles of the conversion of **1a** and the yields of intermediate and **2a**. Reaction conditions were as follows until otherwise stated: 0.5 mmol of **1a**, 0.25 mmol of [Bmim][OAc] and 0.5 mmol of [Bmim][Tf_2N], 0.1 MPa CO_2, 100 °C, different reaction times. Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trioxane as an internal standard.



Scheme 2 The detail reaction route for the synthesis of 3.4.5-trisubstituted oxazolones from CO_2 and propargylic amines.

Table 4 The effect of ILs on the isomerisation step of the intermediate.[a]

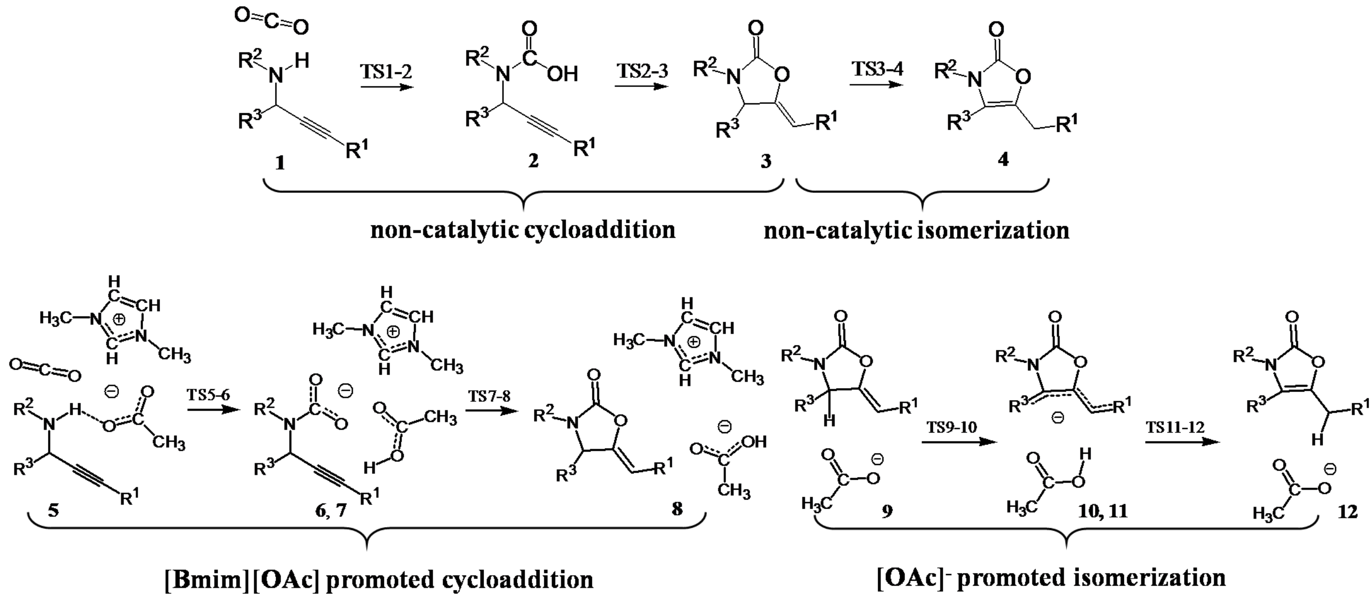


Entry	ILs	t/h	C[b]/%	Y[b]/%
1	--	12	0	0
2	[Bmim][Tf_2N]	12	0	0
3	[Bmim][OAc]	5	99	98
4[c]	[Bmim][OAc]/[Bmim][Tf_2N]	8	99	98
5	[Bmim][OAc]	2	91	90
6	[Omim][OAc]	2	93	92
7	[Emim][OAc]	2	96	94
8	[DBUH][OAc]	2	99	99

[a] t = time, C = Conversion, Y = Yield. Typical reaction conditions were as follows until otherwise stated: 0.5 mmol of intermediate, 0.25 mmol of IL, 0.1 MPa N_2, 100 ℃. [b] Conversion and yield were determined by ^{1}H NMR spectroscopy using 1,3,5-trioxane as an internal standard. [c] 0.25 mmol [Bmim][OAc] and 0.5 mmol [Bmim][Tf_2N] as the catalyst.

For each of the reactions, we found that the propargylic amine could be converted completely in a shorter time. But a much longer time was required to reach satisfactory selectivity of the desired product. Figure 1 shows the time profiles of the conversion of **1a** and the yields of the intermediate and **2a**. **1a** was almost completely converted into the intermediate within 1 h, while complete transformation of the intermediate needed a much longer time. This is a typical phenomenon that a reactant is converted into the product via intermediate. In this work, we studied the reaction of CO_2 and **1a** in detail. ^{1}H and ^{13}C NMR analysis confirmed that the intermediate formed was 5-benzylidene-3-butyl-4-phenyloxazolidin-2-one, which is consistent with the results in the literature.[53] Therefore, we deduced that the synthesis of 3.4.5-trisubstituted oxazolones from propargylic amines and CO_2 contained two steps, cycloaddition and isomerization, as shown in Scheme 2.

As discussed above, [Bmim][OAc] and [Bmim][Tf_2N] had a synergistic effect for achieving high yields of the products. In order to clarify their roles in the reactions, we studied their effects on the second step of the reaction. The results for the transformation of the intermediate into the product (**2a**) are presented in Table 4. Clearly, whether in the presence [Bmim][Tf_2N] or not, the reaction did not occur (entries 1-2). For the IL mixture [Bmim][OAc]/[Bmim][Tf_2N], [Bmim][OAc] acted as the catalyst in the reaction and [Bmim][Tf_2N] had negative effect on the transformation of the intermediate, which may result from the dilution effect. It can be deduced from the results in Tables 1.2.4 that [Bmim][OAc] acted as the catalyst for the two steps of the reaction, while [Bmim][Tf_2N] plays a positive role in inhibiting the side reaction of the first step. At the same time, Figure S4 showed the ^{1}H NMR characteristic peak of chalcone. Through the ^{1}H NMR spectroscopy we can see that with the addition of [Bmim][Tf_2N], the content of chalcone decreased considerably in which its characteristic peak in 8.03 ppm could be hardly seen. So it can be concluded that [Bmim][Tf_2N] inhibits the formation of chalcone. Therefore, high yield of the products could be obtained. Furthermore, some other ILs with [OAc]$^-$ had been investigated (entries 5-8, Table 4). The catalytic performances of 1,3-dialkylimidazolium ILs with different cations were similar (entries 5-7, Table 4). [DBUH][OAc] showed the highest catalytic activity for the second step (entry 8, Table 4). However, the result in Table 1 (entry 8) showed that the yield of the product in the reaction of CO_2 and propargylic amine was only 40% at the complete conversion of propargylic amine. This indicates that [DBUH][OAc] accelerated the side reaction in the first reaction step more effectively.



Scheme 3 The proposed mechanism of the non-catalytic and the catalyst promoted reaction of propargylic amine and CO_2.

To obtain a more comprehensive understanding to the new reactions and reveal the catalytic essence of [Bmim][OAc], we carried out density functional theory (DFT) study using the Gaussian 09 package.[54] Initially, the non-catalyzed reaction of CO_2 and propargylic amine (**1a**) was studied, and the potential energy curve is illustrated (Figure S5). The mechanism of the non-catalytic reaction is shown in Scheme 3. Firstly, CO_2 attacks on the amino group to generate a carbamic acid compound (structure 2). The second step is the formation of the intermediate product (structure 3) via intramolecular cyclic step of structure 2. Finally, the double-bond isomerization gives the final product 3,4,5-trisubstituted oxazolone (structure 4). Figure S5 shows clearly that the intramolecular cyclic step with the overall energy barrier of 61.6 kcal·mol^{-1} (via TS2-3) is the rate-determining step of the cycloaddition. The overall energy barrier of the subsequent isomerization of the intermediate via TS3-4 is 85.0 kcal·mol^{-1}, which is the rate-determining step of the reaction shown in Scheme 1. The energy barriers of both cycloaddition and isomerization steps are too high without catalyst, which is consistent with the experimental results that

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the reactions did not occur without the catalyst (entry 1 in Table 1 and entry 1 in Table 4).

Based on theoretical calculation, we proposed [Bmim][OAc] catalytic mechanism of the reaction, which is presented in Scheme 3. The potential energy curves of the catalyzed cycloaddition and isomerization are illustrated in Figure S6 and S7, respectively. There are two steps in the [Bmim][OAc] promoted cycloaddition. In the first step, with the proton hydrogen of the amino group captured by the $[OAc]^-$ of [Bmim][OAc], the CO_2 electrophilic attack on the amino group becomes much easier, and the energy barrier is only 11.3 $kcal \cdot mol^{-1}$. After this step an acetic acid molecule and a carbamate anion are formed (structure 6). For the subsequent intramolecular cyclic step, due to the proton transfer from acetic acid molecule to the C≡C bond, the attack of O atom on the C atom in the C≡C bond becomes more favorable with an energy barrier of 27.2 $kcal \cdot mol^{-1}$. Via transition state TS7-8 the intermediate is obtained and the catalyst [Bmim][OAc] is regenerated. For the [Bmim][OAc] promoted cycloaddition, the rate determining step is still the intramolecular cyclic step. However, the overall energy barrier of the [Bmim][OAc] catalyzed cycloaddition is reduced to 27.2 $kcal \cdot mol^{-1}$. The mechanism in Scheme 3 illustrates that $[OAc]^-$ promoted the CO_2 electrophilic attack and the intramolecular cyclic step by changing the migration of H.

In the above theoretical calculation, the imidazole cation balanced the charge and has no other obvious catalytic effect for the [Bmim][OAc] promoted cycloaddition. On the other hand, the experimental results in Table 4 (entry 2) shows that both imidazole cation and bis((trifluoromethyl)sulfonyl)imide anion had no catalytic activity for the second step. Furthermore, 1,3-dialkylimidazolium ILs with different cations had similar activity for the isomerisation step (entries 5-7, Table 4), which also suggested that the imidazole cation has less effect on catalytic performance. Thus, only the effect of $[OAc]^-$ has been considered in the subsequent mechanism study for the isomerization of the intermediate. In the $[OAc]^-$ promoted isomerization, it is worth noting that after the intermediate lost the H, a large conjugate structure with negative charge appears (structure 10), in which the substituent R^3 participates in the large conjugate structure. The overall energy barrier of the $[OAc]^-$ promoted isomerization of the intermediate is 17.2 $kcal \cdot mol^{-1}$, which is much lower than that of the non-catalyzed isomerization (85.0 $kcal \cdot mol^{-1}$). $[OAc]^-$ acts as a proton bridge and promotes the H transfer in the isomerization of the intermediate. As a result, the reaction paths are altered, making the reaction much easier. The $[OAc]^-$ promoted mechanism in Scheme 3 can explain the order of the reactivity of the propargylic amines **1d**>**1a**>**1c**>**1b** (Table 3). In the $[OAc]^-$ promoted isomerization, changing the path of H transfer leads to the formation of the large conjugated structure with negative charge. The substituent R^3 plays a special role in this process. So the isomerization ability of the intermediate increases with the increasing electron-withdrawing and conjugation ability of the substituent R^3. The p-chlorophenyl is a good electron-withdrawing group, and therefore **1d** shows highest reactivity among the studied substrates. On the contrary, n-propyl has no use to form the large conjugate structure, and **2i** cannot be formed.

Conclusion

In conclusion, we have discovered a new route to transform CO_2, *i.e.*, CO_2 can react with propargylic amines to form 3,4,5-trisubstituted oxazolones. The [Bmim][OAc]/[Bmim][Tf_2N] mixture is very active, selective, and stable catalyst and solvent for this type of reactions at atmospheric pressure of CO_2. Moreover, the separation of the products from the ILs mixture was very easy, and the ILs mixture could be reused at least five times without considerable loss in catalytic activity and selective. Experimental and theoretical studies reveal that the reaction involves the initial formation of the intermediate via cycloaddition, followed by the isomerization of the intermediate. The catalytic essence of [Bmim][OAc] is that $[OAc]^-$ changes the migration of H, which makes the steps of CO_2 electrophilic attack, intramolecular cyclic and double-bond isomerization be facile. We believe that this route to convert CO_2 has great potential of industrial application because of its obvious attractive advantages.

Experimental

General

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.99%. All solvents and substances were obtained commercially and were used as received. The ILs were supplied by Lanzhou Institute of Chemical Physics; Chinese Academy of Sciences and dried at 70 °C under vacuum for 24 h before used. Standard column chromatography was performed on 20-40 μm silica gel using flash column chromatography. NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). Deuterated solvents chloroform-D (D, 99.8% +3% v/v TMS), deuterium oxide (D, 99.9%) were purchased from Cambridge Isotope Laboratories, Inc., and were used without further purification.

Typical procedure for the preparation of propargylic amines

The procedures were the same as that reported in the literature.[53] CuI (0.6 mmol) was charged in a test tube with a magnetic stirrer. The test tube was sealed and flushed with N_2 and then was charged with alkyne (2 mmol), aldehyde (2 mmol), and amine (2 mmol). The test tube was then placed in an oil bath of 75 ℃ and was allowed to stir overnight. The crude reaction mixture was further purified by silica gel column chromatography to provide the desired propargylic amine.

The procedure for the preparation of the intermediate

The procedure described in the literature.[53] In a sealable test-tube equipped with a magnetic stir bar was charged with CuI

(51.0 mg, 0.268 mmol), benzaldehyde (0.09 mL, 0.900 mmol), butylamine (0.09 mL, 0.900 mmol), phenylacetylene (0.1 mL, 0.892 mmol). The reaction vessel was sealed and attached with a balloon of CO_2. The test-tube was placed in an oil bath of 75 ^oC and was allowed to stir overnight. The reaction mixture was allowed to cool to room temperature and was placed through a plug of silica gel. The crude reaction mixture was further purified by silica gel column chromatography (EtOAc:petroleum ether = 1:30) to provide the desired intermediate as a white yellow solid.

Typical procedure for the synthesis of 3,4,5-trisubstituted oxazolones

As an example, the procedure using **1a** as the substrate was described, and those for other substrates were similar. **1a** (0.5 mmol, 0.1315 g), [Bmim][OAc] (0.25 mmol, 0.0496 g) and [Bmim][Tf_2N] (0.5 mmol, 0.2097 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 an oil bath of 100 ^oC and the reaction mixture was stirred for 12 h. After the reaction, the reactor was placed in ice water for 20 minutes and was placed through a plug of silica gel. The crude mixture was purified by silica gel column chromatography (EtOAc:petroleum ether = 1:20) to provide the desired oxazolone **2a** (128.9 mg, 0.42 mmol, 84%) as a colorless oil

Theoretical methods

All calculations were performed with the Gaussian 09 package. Density functional theory (DFT) was employed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP). Pople style basis sets 6-31+G(d) and 6-311+G(d,p) were used for all atoms. Geometry optimizations and frequency calculations were carried out at the 6-31+G(d) level, and intrinsic reaction coordinate (IRC) calculations were performed to confirm that a given transition state connect a particular couple of consecutive minima. Energies were recalculated at the 6-311+G(d,p) level.

Acknowledgements

The authors thank the National Natural Science Foundation of China. This work was supported by National Natural Science Foundation of China (21303224, 21173239, 21133009, U1232203), and Chinese Academy of Sciences (KJCX2.YW.H30).

Notes and references

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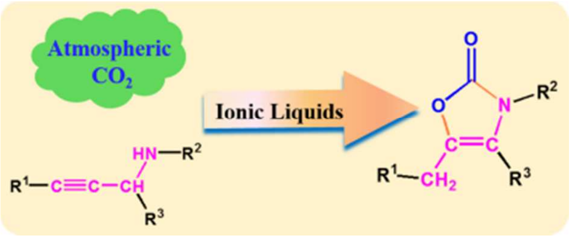

CO_2 can react with various propargylic amines to form 3,4,5-trisubstituted oxazolones catalyzed by the active, selective and stable ionic liquids.