Catalysis Science & Technology

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C5CY01892G

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Organic base/benzyl bromide: an efficient catalytic system for chemical fixation of CO_2 into cyclic carbonates under metal- and solvent-free conditions

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A simple, mild, and inexpensive catalytic system consisting of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and benzyl bromide was developed for the cycloaddition of epoxides with ambient CO_2 under metal-free and solvent-free conditions. Moreover, a wide range of epoxides was converted to the corresponding cyclic carbonates with good-to-excellent yields (81-95%).

Introduction

The exhaustion of carbon-based feedstocks from fossil fuels will occur in decades to come.[1] Thus, employing renewable resources is a key technology for a sustainable society. CO_2 fixation and conversion techniques show great promise for the recycling of CO_2 into valuable chemicals due to the fact that CO_2 is an abundant, sustainable, nontoxic, and renewable C1 feedstock for organic synthesis.[2] However, many challenges must be overcome to increase its value as a chemical feedstock, because the inherent kinetic and thermodynamic stability of CO_2 hampers the development of high-performance catalysts that effect CO_2 activation and transformation.[3]

The development of an efficient chemical process for the chemical fixation of this greenhouse gas into value-added organic chemicals under mild, metal-free reaction conditions is currently a very attractive prospect from the viewpoint of sustainability and green chemistry. Many efficient methods for transformation of CO_2 have emerged,[4] but the atom-efficient addition of CO_2 to epoxides to form cyclic carbonates is one of the most effective strategies. Cyclic carbonates are widely applied in industry and commerce. They are used as monomers in polymerization reactions (producing polycarbonates and polyurethanes), green polar aprotic solvents, fuel additives, constituents of oils and paints, and electrolytes in lithium-ion batteries. They are also important intermediates for pharmaceuticals in biomedical applications.[5]

Many types of catalysts, including alkali metal halides,[6] metalloporphyrin[7] or metallosalen complexes,[8] ionic liquids,[9] quaternary ammonium[10] or phosphonium salts,[11] and *N*-heterocyclic carbenes[12] have been investigated as both single catalysts and co-catalysts to promote the cycloaddition of epoxides to CO_2. However, these systems often suffer from low catalyst activity, the presence of solvents and toxic metals, the need for harsh reaction conditions, and/or expensive multistep catalyst preparation.

To overcome the thermodynamics of CO_2, the use of organic bases has recently emerged. Among these materials, superbases, which provide new opportunities for CO_2 activation, are attracting ever-increasing attention in green chemistry.[13,14] Organic bases have recently been used in the conversion of CO_2 into cyclic carbonates works such as those by the groups of Shi (T= 100-120 °C, pCO_2 = 35 atm),[14a,b] Zhang (T= 120 °C, pCO_2 = 20 atm),[14d] and Chung (T= 80 °C, pCO_2 = 1 atm)[14e]. However, high CO_2 pressures or metallic ions are still required. Thus, metal-free synthetic methods using CO_2 under low pressure (optimally at 1 atm) are still highly desired.

Recently, we reported the efficient benzyl bromide/DMF-catalyzed conversion of CO_2 and epoxides to cyclic carbonates under mild and metal-free conditions (1 atm, 120 °C),[15] but to realize the reaction at low temperature is still a great challenge.

Herein, we present a one-pot process for the combination of benzyl halides and organic bases as catalytic systems for the cycloaddition of epoxides to ambient CO_2. The reaction affords five-membered cyclic carbonates without the need for organic solvents or metal catalysts. This procedure has a broad substrate scope, and represents an efficient, simple, mild, and cost-effective route to the synthesis of cyclic carbonates from CO_2.

Results and discussion

To investigate the effects of organic bases and halides on the CO_2 conversion, several typical organic bases (Scheme S1,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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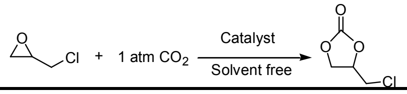
DOI: 10.1039/C5CY01892G

see ESI) and halides were selected and explored. The bases were 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), *N*,*N*-dimethylaminopyridine (DMAP), pyridine (Py), triethylamine (TEA), imidazole (Im), and *N*-methylimidazole (MIm).

Table 1 Optimization of reaction conditions[a]



Entry	Catalytic system (mol)	T(°C)	Time (h)	Yield[b](%)
1	5% DBU	65	24	48
2	5% PhCH$_2$Br	65	24	0
3	5% PhCH$_2$Br + 5% DBU	65	24	95
4	5% PhCH$_2$Br + 10% DBU	65	24	96
5	2.5% PhCH$_2$Br + 5% DBU	65	24	64
6	5% PhCH$_2$Br + 5% DBU	45	24	85
7	5% PhCH$_2$Br + 5% DBU	25	24	54
8	5% PhCH$_2$Br + 5% DBU	65	22	95
9	5% PhCH$_2$Br + 5% DBU	65	20	89

[a] Reaction conditions: epichlorohydrin (6 mmol), CO$_2$ (99.999%, balloon). [b] Isolated yield

First, the superbase DBU was employed in combination with benzyl bromide to systematically study the effect of various parameters on the model reaction of epichlorohydrin and CO$_2$ to produce the cyclic carbonate (chloromethyl)ethylene carbonate. The corresponding results are summarized in Table 1. At ambient CO$_2$ pressure, 5 mol% DBU alone afforded the corresponding cyclic carbonate in 48% yield (entry 1, Table 1), which might be due to the nucleophilic capability of DBU and its CO$_2$ activation effect.[16] When only benzyl bromide was used as the catalyst, negligible yield was observed (entry 2). However, a combination of DBU and benzyl bromide realized a significant enhancement in catalytic activity (95%, entry 3) compared to that of each component individually, indicating the highly positive synergistic effect of DBU and benzyl bromide. No increase in the product yield was observed upon increasing the amount of DBU from 5 to 10 mol% (entries 3 and 4). However, an obvious decrease in the yield was observed when the amount of benzyl bromide decreased to 2.5 mol% (64%, entry 5), indicating that 5 mol% of DBU/benzyl bromide was the optimal catalyst loading. Additionally, upon lowering the temperature to 45 °C, a moderate yield (85%, entry 6) was obtained. However, further decrease of the temperature from 45°C to 25 °C leads to an unsatisfactory yield (54%, entry 7). Thus, 65 °C was selected as the optimal temperature.

In addition, the time dependence of product yield was also evaluated. As shown in Fig. 1, it can be seen that reaction time has a significant influence on the reaction yield, and that the cycloaddition reaction proceeds rapidly within the first 10 h, during which time the product yield increases from 0 to 74%. Further extending the reaction time results in relatively little improvement, because the concentration of starting materials decreases gradually with reaction time. As a result, reaction times of 22 and 24 h give almost the same yield of 95%, but a slightly lower yield of 89% is observed when the reaction time is 20 h (Fig. 1; entries 3, 8, and 9, Table 1). Hence, 22 h was chosen as the optimum reaction time. Moreover, the selectivity of the reaction for the desired product remained above 99% throughout.

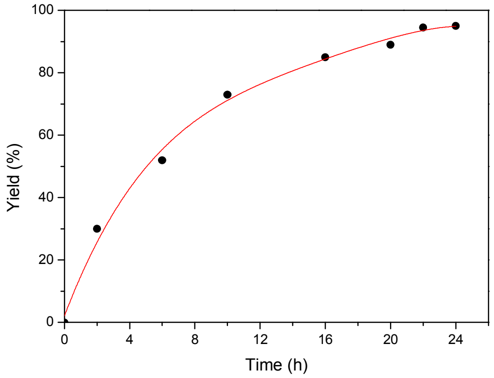


Fig. 1 Dependence of product yield on reaction time[a]

[a] Reaction conditions: epichlorohydrin (6 mmol), PhCH$_2$Br (0.3 mmol), DBU (0.3 mmol), CO$_2$ (99.999%, balloon), isolated yield.

Table 2 The effect of organic bases on the cycloaddition[a]

Entry	Base	pKa[b]	T(°C)	Yield[c](%)	TON[d]
1	DBU	24.3	65	95	19.0
2	DBN	23.7	65	91	18.2
3	DMAP	18.0	65	83	16.6
4	DABCO	(8.7)	65	54	10.8
5	Pyridine	12.5	65	85	17.0
6	TEA	18.8	65	84	16.8
7	MIm	(7.1)	65	81	16.2
8	Im	(7.0)	65	75	15.0

[a] Reaction conditions: epichlorohydrin (6 mmol), PhCH$_2$Br (0.3 mmol, 5 mol%), time 22h, CO$_2$ (99.999%, balloon). [b] The pKa value of the conjugated acid in acetonitrile or water (in parentheses)[14d,g] [c] Isolated yield (average of 2 runs). [d] TON: turnover number (in 22 hours).

Table 2 shows the effects of the different organic bases employed on the reaction in the presence of 5 mol% benzyl bromide. It can be seen that DBU is the most effective among the organic bases (entry 1, Table 2). Heldebrant *et al*. reported that organic bases with a lower p*K*a value possess a lower negative Gibbs free energy to activate CO$_2$.[16a] Consequently, the ability of the organic bases to form carbamate salts with CO$_2$ is in accordance with the order of the p*K*a values. Notably, the results in Table 2 are largely consistent with this order. However, the presence of DABCO affords an unsatisfactory result (entry 4), which might be related to its high steric hindrance due to its rigid spherical shape. The results indicate that the strength of the base is a key factor for its catalytic activity in the reaction, and that steric hindrance of the base is also an important factor.

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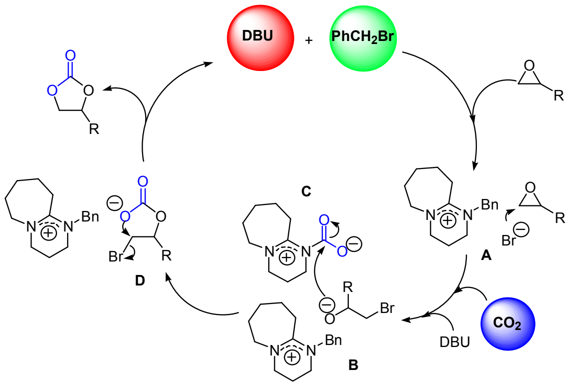
Based upon previous mechanistic studies on related systems[14a,17,19] and the above results, we propose a plausible mechanism, as shown in Scheme 1. It is known that benzyl halides can react with organic bases easily to form quaternary onium salts. In the present DBU/$PhCH_2Br$ system, the aminidinium salt Bn-DBU^+Br^- (**A**) is initially formed and catalyzes the ring-opening reaction through nucleophilic attack of its bromide ion at the less sterically hindered β-carbon atom of the epoxide, which results in oxy anion species **B**. Simultaneously, DBU coordinates reversibly with CO_2,[14f] affording carbamate salt **C**, affording an activated form of CO_2. Subsequently, nucleophilic attack by **B** on **C** forms alkylcarbonate anion **D**. Finally, the ring-closing of intermediate **D** affords the corresponding cyclic carbonate and regenerates the catalyst; thus the catalytic cycle is completed. According to this mechanism, when salt **C** is formed from DABCO and CO_2, the approach of **B** should be hindered due to its ball-like shape, leading to the lower yield observed in this system.



Scheme 1. Proposed mechanism for the coupling reaction of epoxide with CO_2 catalyzed by $PhCH_2Br$ and DBU.

To investigate the reaction mechanism in detail, kinetic studies of the catalytic conversion of CO_2 and epichlorohydrin to cyclic carbonate were carried out using $PhCH_2Br$ and DBU as co-catalysts. As shown in Fig. 1, the product yield and reaction time almost have a linear relationship in the first 4 hours. Thus, the first 3 hours were chosen to investigate the reaction. The resulting kinetic curves of three different concentrations of DBU on the reaction are shown in Fig. 2. Notably, the concentration of DBU has a positive effect on the reaction rate, indicating the important step of DBU coordinates reversibly with CO_2 to afford carbamate salt **C** in the proposed mechanism (Scheme 1). However, when using the excess amount of DBU (10 mol%; $PhCH_2Br$: 5 mol%), no drastic increase in the reaction rate was observed (line B and line C). This behaviour may indirectly indicate that the step of forming CO_2 activated species by DBU (**C**, Scheme 1) is not the rate-determining step in the proposed mechanism. Additionally, the kinetic curves of three different concentrations of $PhCH_2Br$ on the reaction were also investigated (Fig. 3). It can be clearly seen from Fig. 3 that the concentration of $PhCH_2Br$ plays a significant role in the reaction. However, when using the excess amount of $PhCH_2Br$ (7.5 mol%; DBU: 5 mol%), no significant increase in the reaction rate was observed. This further indicates the important role of the initially formed complex of DBU and $PhCH_2Br$ (Bn-DBU^+Br^- (**A**)) in the catalytic cycle, that is, the ring-opening reaction is through nucleophilic attack of its bromide ion on the epoxide rather than sole $PhCH_2Br$.

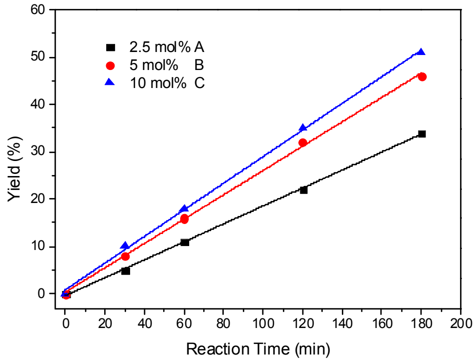


Fig. 2 Effect of DBU concentration on the reaction[a].

[a] Reactions were carried out under 1 atm CO_2 without solvent. Epichlorohydrin 6 mmol, $PhCH_2Br$ 5 mol%, T = 65 °C, isolated yield. Line A: n[DBU] = 2.5 mol%, y = 0.1893x, R^2 = 0.9997; line B: n[DBU] = 5 mol%, y = 0.2569x, R^2 = 0.9988; line C: n[DBU] = 10 mol%, y = 0.2810x, R^2 = 0.9986.

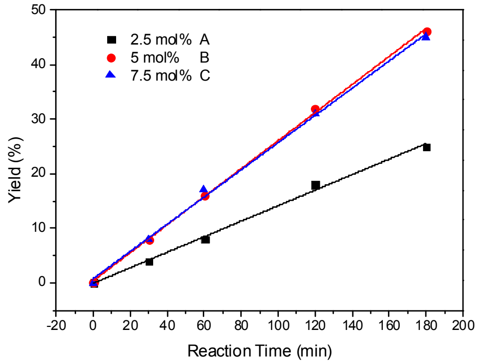


Fig. 3 Effect of DBU concentration on the reaction[a].

[a] Reactions were carried out under 1 atm CO_2 without solvent. Epichlorohydrin 6 mmol, DBU 5 mol%, T = 65 °C, isolated yield. Line A: n[$PhCH_2Br$] = 2.5 mol%, y = 0.1422x, R2 = 0.9952; line B: n[$PhCH_2Br$] = 5 mol%, y = 0.2569x, R2 = 0.9988; line C: n[$PhCH_2Br$] = 7.5 mol%, y = 0.2499x, R2 = 0.9971.

The present results (entries 1, 3, and 5, Table 1) and the above mechanism indicate that the role of the halide anion is important to the reaction rate. It is known that the order of nucleophilicity is Cl^- > Br^-, while the order of leaving ability is Br^- > Cl^-. Thus, the balance between the two conflicting factors is important. The proposed mechanism also indicates that the nucleophilicity of **A** and the leaving ability of halide anions from **D** are important for the catalytic activity. Hence, we investigated the effect of the halide anions on the catalytic activity, and the results are summarized in Table 3.

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Table 3 The effect of halides on the cycloaddition[a]

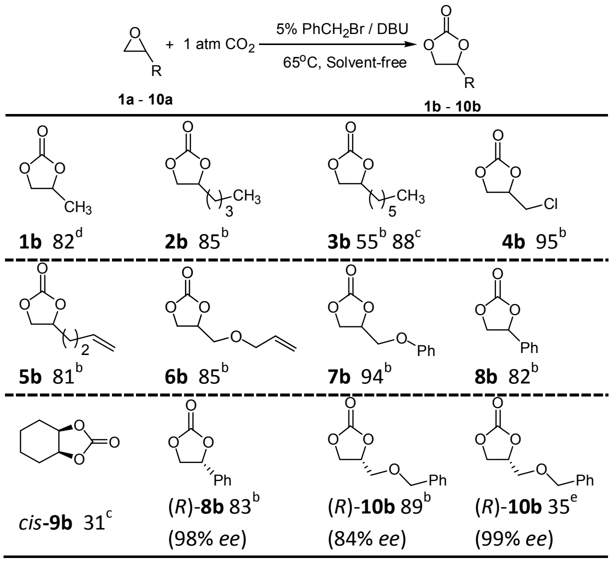
Entry	Halide	Yield[b]%	TON[d]
1	$PhCH_2Br$	95	19.0
2	$PhCH_2Cl$	71	14.2
3	p-$^tBuPhCH_2Br$	92	18.4
4	4-Nitrobenzyl bromide	83	16.6
5	α-Bromodiphenylmethane	86	17.2
6	$CH_3CH_2CH_2CH_2Br$	68	13.6
7	$CH_3CH_2CH_2CH_2I$	27	5.4
8	$n$$Bu_4NBr$	72 (58)[c]	14.4

[a] Reaction conditions: epichlorohydrin (6 mmol), DBU (0.3 mmol, 5 mol%), CO_2 (99.999%, balloon), T= 65 °C, time 22h. [b] Isolated yield (average of 2 runs). [c] without of DBU. [d] TON: turnover number (in 22 hours).

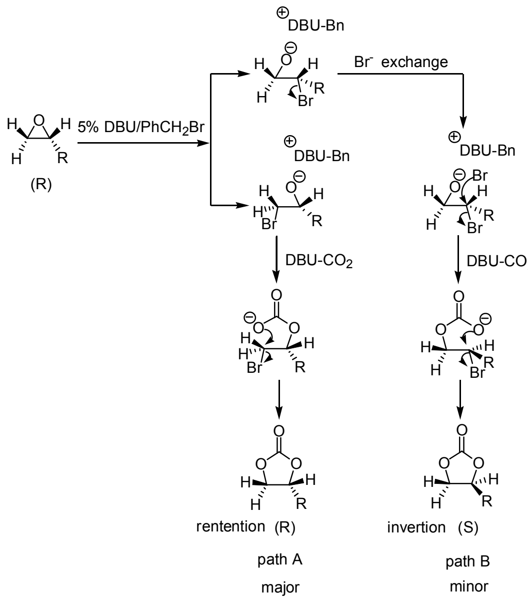
It can be seen that the activity increased in the order $Cl^- < Br^-$ (entries 1 and 2, Table 3). Additionally, the benzyl bromide derivatives with an electron-donating group gave better results than those with an electron-withdrawing group (entries 3, 4, and 5), presumably due to electron-withdrawing groups decreasing the leaving ability of the bromide anion from the aminidinium center. Notably, in the presence of benzyl bromide, the reaction yield was better than those in the presence of p-$^tBuPhCH_2Br$ and α-bromodiphenylmethane (entries 1, 3, and 5), indicating that the bulkiness of the formed quaternary onium salts also affected the reaction. When the arylmethyl halide is replaced by an alkyl halide, the yield decreases significantly (entries 6 and 7). For comparison with the ammonium salts formed using arylmethylbromide derivatives, $n$$Bu_4NBr$ was employed as the bromide anion donor under the same conditions as the model reaction (entry 8). However, the yield was significantly lower than that using benzyl bromide as the bromide anion source, which is presumably due to the electrostatic interaction between the bromide anion and the ammonium center decreasing with the bulkiness of the cation.[17] Thus, the nucleophilicity of the bromide anion is weaker for $n$$Bu_4NBr$ than the salts (Bn-DBU^+Br^-).

In order to examine the substrate scope of the present dual catalyst system, a wide range of epoxides were investigated under the optimal reaction conditions (Table 4). The results show that diverse epoxides are converted to the corresponding cyclic carbonates under ambient conditions with good-to-excellent yields. Among them, epichlorohydrin **4a** gave the best result, probably due to the electron-withdrawing properties of the chlorine atom. Similarly, the epoxides with an oxymethylenemoiety (**6a**, **7a**, and **10a**, Table 4) afforded higher yields than those with alkyl groups. These substituents resulted in facilitated nucleophilic attack at the epoxide ring carbon atoms. Additionally, the other functional groups on the epoxide were stable in the reaction, indicating the outstanding efficiency of the catalytic system. The epoxides with large steric hindrance (**2a**, **3a**, and **8a**) were also converted to the corresponding carbonates in good yields. Due to the higher steric hindrance of epoxide **3a** compared to the other epoxides, a higher reaction temperature (95 °C) was necessary to obtain a higher product yield. On the other hand, cyclohexene oxide, which is known to perform cycloaddition with CO_2 poorly due to its steric hindrance, was converted to the corresponding carbonate **9b** in 31% yield at 95 °C, which was confirmed exclusively the *cis* isomer by ^1H NMR and ^{13}C NMR spectra.[18]

Table 4 Cycloaddition of CO_2 to various epoxides catalyzed by $PhCH_2Br/DBU$[a]



[a] Reaction conditions: epoxide (6mmol), binary catalyst (5 mol%), CO_2 (99.999%, balloon), reaction time 22 h, isolated yield. [b] T = 65 °C. [c] T = 95 °C. [d] Experiment reacted in 6M toluene, T = 45 °C. [e] DBU as a sole catalyst, T = 65 °C.



Scheme 2. Possible reaction pathways for the partial conversion of configuration.

This commercially inexpensive catalytic system can also be applied in the coupling of CO_2 and enantiomerically pure

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epoxides. (*R*)-**8a** was transformed to (*R*)-**8b** in 98% enantiomeric excess (*ee*), while (*R*)-**10b** was obtained with some loss in optical purity (84% *ee*) (Table 4). It can be concluded that reaction at the β-carbon of epoxide seems favorable (Scheme 2, path A). Epoxide (*R*)-**10a** has lower potential steric hindrance and higher reactivity than (*R*)-**8a**; thus, as for (*R*)-**10b,** the *ee* loss may be attributed to the nucleophilic attack on the α-carbon of the epoxide by the bromide anion, which may also be followed by a bromide-bromide ion exchange process to eventually afford the (*S*)-**10b** product (Scheme 2, path B).[19] When only DBU was used as a catalyst, (*R*)-**10b** was obtained in 35% yield, but with retention of stereochemistry (>99% *ee*), which indicates that direct nucleophilic attack of carbamate salt **C** on the epoxide proceeds exclusively at the less sterically hindered carbon atom.[12a,b] This further demonstrates the possible role of the bromide anion in path B for the ring-opening process.

Conclusions

In summary, a simple, inexpensive and efficient binary organocatalytic system consisting of DBU and benzyl bromide was developed for the synthesis of cyclic carbonates from epoxides and CO_2 under metal- and solvent-free conditions. A diverse range of epoxides was transformed into the corresponding cyclic carbonates with good-to-excellent yields (81-95%) under very mild conditions (65 °C, 1 atm CO_2). Furthermore, optically pure epoxides were also investigated, and a plausible mechanism for the coupling reaction of epoxide with CO_2 was proposed. The proposed protocol provides an example of an easily handled, commercially viable, and environmentally benign alternative for chemical fixation of CO_2 into 5-membered cyclic carbonates.

Experimental section

All starting materials and solvents commercially available were purchased at the highest quality from Sigma-Aldrich or Wako and used as received unless otherwise indicated. Chemical yields refer to the pure isolated substances. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained using a Brucker AV-500 (500 MHz) spectrometer. The chemical shifts of the products were reported in ppm with reference to Me_4Si as the internal standard in $CDCl_3$ solution. Enantiomeric excesses of the carbonates were determined by HPLC analyses with a Daicel Chiralcel OD-3 with detection at 254 nm.

Representative procedure for the cyclic carbonate formation (**4b**): In a 20 mL two-neck flask, epichlorohydrin **4a** (6 mmol, 0.555 g), DBU (5 mol%, 0.046g) and $PhCH_2Br$ (5 mol%, 0.051g) were added under N_2 gas and then stirred at 65 ^{o}C for 22 h under an atmosphere of CO_2 (99.999%, balloon). After completion, the reaction mixture was purified by column chromatography (hexane:ethyl acetate = 1:1) to afford the desired cyclic carbonate 0.778g (yield: 95.0%).

^{1}H NMR (500 MHz, $CDCl_3$): 5.12–5.01 (m, 1H), 4.69–4.55 (m, 1H), 4.48–4.35 (m, 1H), 3.89 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.77 (dd, *J* = 12.5, 3.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 154.8, 74.7, 67.0, 44.6. All the data are consistent with that previously reported. See the Supporting Information for characterization data of other compounds.

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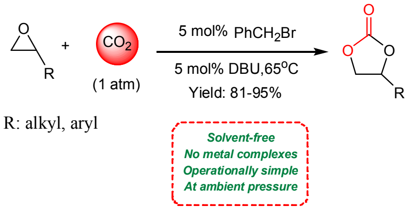
View Article Online
DOI: 10.1039/C5CY01892G

Graphical Abstract

Organic base/benzyl bromide: an efficient catalytic system for chemical fixation of CO_2 into cyclic carbonates under metal- and solvent-free conditions



A simple, mild and inexpensive catalytic system consisting of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and benzyl bromide was developed for the cycloaddition of epoxides to ambient CO_2 under metal-free and solvent-free conditions. Moreover, a wide range of epoxides was converted to the corresponding cyclic carbonates with good-to-excellent yields (81-95%). The proposed protocol provides an example of an easily handled, practical, and environmentally benign alternative for chemical fixation of CO_2 into 5-membered cyclic carbonates.