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Ionic liquid [DBUH][BO_2]: an excellent catalyst for chemical fixation of CO_2 under mild conditions†

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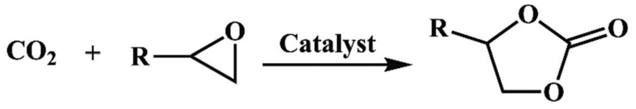
The green basic IL **[DBUH][BO_2]** was easily synthesized for the first time and used to catalyze the cycloaddition of CO_2 and epoxides under solvent- and halogen-free conditions at atmospheric pressure and room temperature with high target product yields. Moreover, this IL could be easily recovered and reused at least five times without activity loss. The basic anion and the cation with N–H had excellent synergistic catalytic effects on promoting these reactions. Particularly, this basic IL, the anion of which had a strong nucleophilic ability, was also very effective for the reactions of CO_2 and 2-aminobenzonitriles into quinazoline-2,4(1*H*,3*H*)-diones, giving the desired products in high yields at atmospheric pressure and room temperature.

Introduction

Compared with toxic phosgene and carbon monoxide, chemical fixation of the abundant, nontoxic, easily available but inert greenhouse gas carbon dioxide (CO_2) into high value-added chemicals has important significance and long-term potential in both academia and industry,[1–3] especially at room temperature and atmospheric pressure of CO_2.[4–6] Among various CO_2-related reactions, the transformation of CO_2 and epoxides to five-membered cyclic carbonates through the formation of a new C–O bond (Scheme 1) occupies an important position,[7,8] not only because the products are important green polar aprotic solvents and intermediates in the fields of chemistry, electricity and medicine,[9,10] but also because this reaction has high atom efficiency without any by-product.[11]

Ionic liquids (ILs), which have some unusual properties including negligible vapor pressure, nonflammability, and designability,[12] are one kind of excellent catalyst for the reactions of CO_2 and epoxides.[13] For example, homogeneous and heterogeneous quaternary ammonium-ILs,[14] functionalized ILs including hydroxyl-ILs,[15,16] urea derivative based ILs,[17] amino acid-based ILs[18,19] and Lewis basic ILs[20] are proposed for this reaction. Although some of the aforementioned ILs showed good catalytic activity, the reaction could proceed at high CO_2 pressure and/or high reaction temperature. In this way, a dual-ionic liquid system [$TMGH^+$][$^-O_2MMIm^+$][Br^-] was reported for use in the cycloaddition of CO_2 and epoxides at atmospheric pressure and low reaction temperature,[21] and the halide ion in this IL was an integral part in the catalytic process. Recently, a halogen-free basic IL [P_{4444}][2-OP] was developed to catalyze these reactions at room temperature efficiently,[22] but the synthetic process of this IL was complex. Therefore, the exploration of an efficient, green and easy-to-prepare IL for this class of reactions at atmospheric pressure and room temperature under halogen- and solvent-free conditions is still highly desirable. Borates including metaborate (BO_2^-), diborate ($B_2O_4^{2-}$), triborate ($B_3O_5^-$), tetraborate ($B_4O_7^{2-}$), pentaborate ($B_5O_8^-$) and hexaborate ($B_6O_{10}^{2-}$) are widely distributed in salt lakes, and research studies are mainly concentrated on the extraction of borate.[23] However, we recently found that the borate anion could efficiently catalyze the reaction of CO_2 and 2-aminobenzonitrile for its strong basicity.[24] Compared with other borates, BO_2^- has stronger basicity and a smaller size, indicating its better catalytic activity for the chemical fixation of CO_2. 1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**) was the superbase and was used to easily synthesize various ILs by regulating the anion *via* neutralization.[25] Recently, the [DBUH] based IL has already



Scheme 1 The green route for the synthesis of cyclic carbonates using CO_2 and epoxides.

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been used to catalyze this kind of reaction. For example, Hou *et al.* developed halogen-free $[DBUH]_3NbO_5$ and used it for the synthesis of cyclic carbonates from epoxides and CO_2 at 130 °C and 3.0 MPa with high activity and selectivity.[26]

Herein, the green and halogen-free basic IL **[DBUH][BO$_2$]** was easily synthesized for the first time and used to catalyze the cycloaddition of CO_2 and epoxides without any solvents at atmospheric pressure and room temperature with high target product yields. Moreover, this IL could be easily recovered and reused at least five times without activity loss. Particularly, this basic IL could also effectively catalyze the reactions of CO_2 and 2-aminobenzonitriles into quinazoline-2,4(1*H*,3*H*)-diones at atmospheric pressure and room temperature with high yields of the desired products.

Experimental

Chemicals

CO_2 was supplied by Tianjin Feilin Gases Co., Ltd with a purity of 99.99%. 1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**) (98%) and 2-amino-5-bromobenzonitrile (99%) were purchased from J&K Scientific Ltd. 2-Amino-5-chlorobenzonitrile (98%) and 2-aminobenzonitrile (98%) were obtained from 3A Chemicals Ltd. Boric acid (99%), metaboric acid (99%) and glacial acetic acid (99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Epichlorohydrin (99%), butylene oxide (98%) and 3-bromo-1,2-epoxypropane (97%) were purchased from Tokyo Chemical Inorganic Co., Ltd. 1,2-Epoxy-3-phenoxypropane (99%) was purchased from InnoChem Co., Ltd. *N*,*N*-Dimethylformamide (AR), dimethyl sulfoxide (AR), *tert*-butyl methyl ether (AR), ethanol (AR) and diethyl ether (AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. Dimethyl sulfoxide-d$_6$ (99.9%) was supplied by Cambridge Isotope Laboratories, Inc. 1-Butyl-3-methylimidazolium nitrate ($[Bmim][NO_3]$), 1-butyl-3-methylimidazolium dicyanamide ($[Bmim][N(CN)_2]$) and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) were supplied by Lanzhou Yulu Fine Chemical Co., Ltd. All the chemicals were used without further purification.

Apparatus

Standard column chromatography was performed on 20–40 μm silica gels using flash column chromatography. NMR spectra were recorded on a Bruker Fourier 400 MHz NMR spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). The elemental analysis was carried out with a Flash EA 1112 elemental analyzer.

Synthesis of [DBUH][BO$_2$]

The IL **[DBUH][BO$_2$]** was synthesized *via* neutralization. In the experiment, methanol (10 mL), **DBU** (10 mmol, 1.5224 g) and HBO_2 (10 mmol, 0.4382 g) were loaded into a 50 mL flask in a 30 °C water bath and the neutralization reaction was allowed to proceed for 24 h. Then, the solvent was removed by rotary evaporation under vacuum at 70 °C, and finally the IL was obtained. This IL was a colourless liquid at room temperature.

Catalytic reaction

As an example, the procedure using epichlorohydrin as the substrate is described, and those for other substrates were similar. Epichlorohydrin (2 mmol, 0.1850 g) and **[DBUH][BO$_2$]** (1.5 mmol, 0.2941 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 constant temperature water bath and the reaction mixture was stirred for a desired time. After the reaction, the reactor was placed in ice water for 20 minutes and the reaction mixture was passed through a plug of silica gel. The crude mixture was purified *via* silica gel column chromatography (EtOAc : petroleum ether = 1 : 15) to obtain the desired cyclic carbonate 4-chloromethyl-[1,3]dioxolan-2-one.

Typical procedure for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones

As an example, the procedure using 2-aminobenzonitrile as the substrate is described, and those for other substrates were similar. In a typical experiment, 2-aminobenzonitrile (2 mmol, 0.2643 g), toluene (1 mL) and **[DBUH][BO$_2$]** (1.5 mmol, 0.2941 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 through 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 30 °C oil bath for the desired time. After the reaction, 25 mL water was added into the reactor and the mixture was centrifuged to precipitate the product. Then the product was washed with *tert*-butyl methyl ether (3 × 15 mL) and ethanol (3 × 15 mL), and then dried at 95 °C for 3 h to obtain the target product.

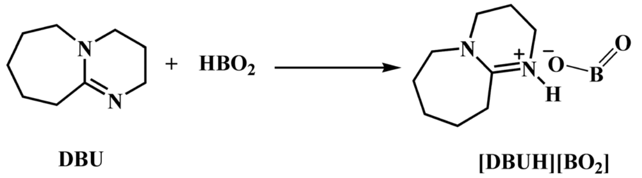
Catalyst recyclability

Epichlorohydrin (2 mmol, 0.1850 g) and **[DBUH][BO$_2$]** (1.5 mmol, 0.2941 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 30 °C water bath and the reaction mixture was stirred for 6 h. After the reaction, the product was extracted by diethyl ether (3 × 2 mL) and the yield was determined *via* ^1H NMR using DMF as the internal standard; in particular, the extraction experiments were conducted under a CO_2 atmosphere and at 0 °C. The IL separated was used directly for the next run after being dried under vacuum at 60 °C for 24 h.

Results and discussion

Ionic liquid [DBUH][BO$_2$]

The IL **[DBUH][BO$_2$][DBUH][BO$_2$][DBUH][BO$_2$]** was synthesized *via* neutralization of 1,8-diazabicyclo[5.4.0]undec-7-ene (**DBU**) and metaboric acid (HBO_2), as shown in Scheme 2. The formation of this superbase-derived IL **[DBUH][BO$_2$]** was shown



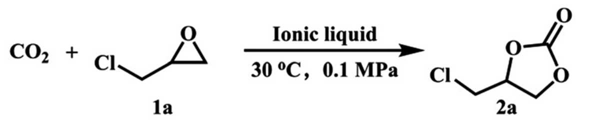
Scheme 2 Preparation of the IL **[DBUH][BO$_2$]**.

via FT-IR spectroscopy (Fig. 1). The broad absorption peak at 3435 cm^{-1} corresponded to the stretching vibration peak of N–H, while the stretching vibration peak of O–H at 3200 cm^{-1} belonging to HBO$_2$ disappeared,[27] suggesting the formation of [DBUH]$^+$. Furthermore, the ^{1}H NMR peaks of **[DBUH][BO$_2$]** agreed well with those of [DBUH]$^+$ in the aprotic IL [DBUH][MIm],[21] which further proved the formation of **[DBUH][BO$_2$]**. The ^{1}H and ^{13}C NMR spectra of the IL **[DBUH][BO$_2$]** are presented in the ESI.† In addition, the elemental analysis of the IL **[DBUH][BO$_2$]** for C, H and N was carried out (calcd: C 55.14, H 8.74, N 14.29; found: C 55.02, H 8.82, N 14.13).

Screening of catalysts

Firstly, the catalytic activities of various halogen-free ILs were investigated using epichlorohydrin (**1a**) as the substrate at room temperature and 0.1 MPa CO$_2$ within 4 h, and the results are given in Table 1. Clearly, the reaction did not proceed in the absence of any of the catalysts (Table 1, entry 1). For imidazolium-based ILs (entries 2–4), the neutral ILs 1-butyl-3-methylimidazolium nitrate ([Bmim][NO$_3$]) and 1-butyl-3-methylimidazolium dicyanamide ([Bmim][N(CN)$_2$]) had little catalytic effects on this reaction, while the basic IL 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) could catalyze the reaction, with the yield of the target product 4-chloromethyl-[1,3]dioxolan-2-one (**2a**) being 42%, suggesting that the basic anion was crucial for the catalytic activity. With this in mind, the basic **DBU**-based IL was used for this reaction, and it was found that the IL 1,8-diazabicyclo[5.4.0]-7-undecenium acetate ([DBUH][OAc]) showed good catalytic activity and gave product **2a** in 68% yield (entry 5), which was much higher than that of [Bmim][OAc]. This result showed that, with the same basic anion, the catalytic activity of the **DBU**-based IL was better than that of the imidazolium-based IL, indicating that [DBUH]$^+$ also had a positive role in this reaction. Therefore, the **DBU**-based ILs 1,8-diazabicyclo[5.4.0]-7-undecenium borate ([DBUH][H$_2$BO$_3$]) and 1,8-diazabicyclo[5.4.0]-7-undecenium metaborate **[DBUH][BO$_2$]**, the anions of which had stronger basicity, were used for this reaction. Interestingly, both ILs showed catalytic activities for this reaction, but the activities were very different with the yields of the target product **2a** being 54% and 91% (entries 6 and 7), respectively. This may be because [H$_2$BO$_3$]$^-$ was so big that too much steric hindrance reduced the activity, while [BO$_2$]$^-$ with strong basicity and an appropriate size showed excellent activity for this reaction (entries 7 and 8).

Table 1 IL-catalyzed reaction of epichlorohydrin (**1a**) and CO$_2$[a]



Entry	IL	Yield[b] (%)
1	—	0
2	[Bmim][NO$_3$]	<5
3	[Bmim][N(CN)$_2$]	<5
4	[Bmim][OAc]	42
5	[DBUH][OAc]	68
6	[DBUH][H$_2$BO$_3$]	54
7	**[DBUH][BO$_2$]**	91
8[c]	**[DBUH][BO$_2$]**	94

[a] The typical reaction conditions were as follows until otherwise stated: 2 mmol of **1a** (0.1850 g), 1.5 mmol of the IL, 0.1 MPa CO$_2$, 30 °C, 4 h. [b] Yields were determined *via* ^{1}H NMR spectroscopy using DMF as the internal standard. [c] The reaction time was 6 h.

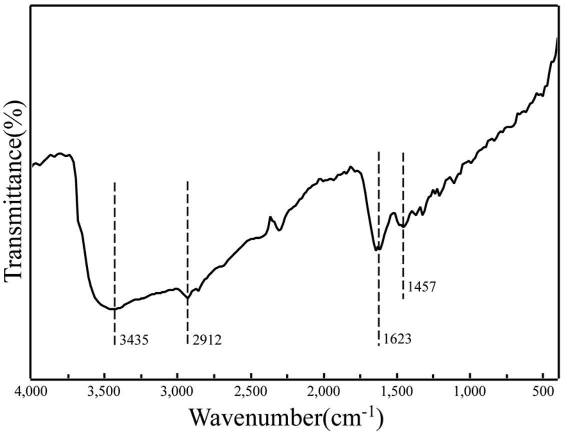


Fig. 1 The FT-IR spectrum of the IL **[DBUH][BO$_2$]**.

Effect of reaction conditions

Subsequently, the effects of different **[DBUH][BO$_2$]** amounts on the yield of **2a** were studied (Fig. 2a), and the results showed that a 75% molar ratio of **[DBUH][BO$_2$]** was enough for the reaction. The effect of reaction time on the yield of **2a** with a 25% molar ratio of **[DBUH][BO$_2$][DBUH][BO$_2$]** was also tested and the results are shown in Fig. S3 (ESI†). The results indicated that, with 25% **[DBUH][BO$_2$]**, this reaction could also proceed smoothly, while a much longer reaction time was needed. Therefore, given the recyclability of the IL and the reaction time, we chose this high IL/substrate ratio (75%) as the optimal condition. Fig. 2b illustrates the dependence of yield on the reaction time. It was found that the yield of **2a** increased with increasing reaction time and could reach 94% in 6 h. Thus, the optimal reaction conditions were obtained (Table 1, entry 8). It can be seen that this easily prepared halogen-free IL is a very excellent catalyst considering that the reaction proceeded without any solvent under mild conditions within a short time.

The reusability of the catalyst

Because the IL can be separated by adding diethyl ether after the reaction, the reusability of **[DBUH][BO$_2$]** was tested, and the

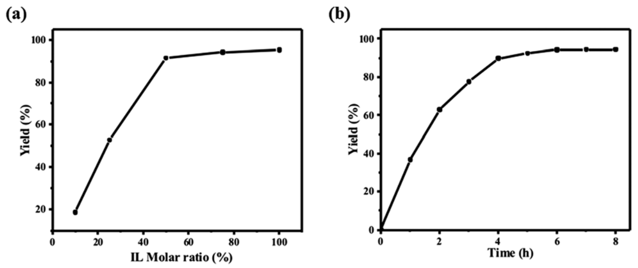


Fig. 2 (a) Dependence of the yield on the amount of **[DBUH][BO$_2$]** in 6 h. Reaction conditions: **1a** (2 mmol, 0.1850 g), CO$_2$ (0.1 MPa), 30 °C and different **[DBUH][BO$_2$]** contents; (b) the effect of reaction time on the yield of **2a** with 75% **[DBUH][BO$_2$]**. Reaction conditions: **1a** (2 mmol, 0.1850 g), CO$_2$ (0.1 MPa), 30 °C and different reaction times. The yield was determined *via* ^{1}H NMR spectroscopy using DMF as the internal standard.

results are shown in Fig. 3. The catalytic activity of the IL did not show any obvious change after it was reused five times, indicating its good recyclability.

In addition, comparison of the catalytic performance between the IL in this work and the reported halogen-free ILs for the reaction of epichlorohydrin and CO$_2$ is shown in Table S1 (ESI†). Compared with [DBUH]$_3$NbO$_5$, the catalytic activity of the IL **[DBUH][BO$_2$]** was much higher. It was also found that the catalytic activity of the IL **[DBUH][BO$_2$]** was no less than that of [P$_{4444}$][2-OP]. Although the amount was much higher, **[DBUH][BO$_2$]** was easy to prepare and recycle.

Reaction mechanism

The results in Table 1 suggest that the basic anion [BO$_2$]$^-$ having a strong nucleophilic ability played an important role in the catalytic activity, while the [DBUH]$^+$ cation also exhibited a catalytic effect. Thus, on the basis of the experimental results of this work and the related knowledge in the literature,[22] we deduced that the IL **[DBUH][BO$_2$]** had an excellent synergistic catalytic effect on the reactions of CO$_2$ and epoxides and a possible mechanism was proposed, which is presented in Scheme 3. Firstly, the [BO$_2$]$^-$ caused a nucleophilic attack on the C atom of CO$_2$ to form the carbamate anion. Because of the strong basicity and nucleophilic ability of [BO$_2$]$^-$, this step proceeded smoothly, and this is why the reactions could proceed at atmospheric pressure of CO$_2$. It was reported that the N–H bond and halide anion had a synergistic activation effect on epoxides to promote its ring-opening.[21,22,27,28] Compared with the halide anion, the O$^-$ of the carbamate anion also had nucleophilic ability. Therefore, in the next step, the O$^-$ of the carbamate anion caused a nucleophilic attack on the less sterically hindered C atom of the epoxide, and at the same time the H atom of the N–H bond belonging to [DBUH]$^+$ interacted with the O of the epoxide through hydrogen bonding to promote opening of the epoxide ring. Then, the O$^-$ of the epoxide that was stabilized by the N–H of [DBUH]$^+$ caused a nucleophilic attack on the C atom of the activated CO$_2$, leading to the formation of cyclic carbonate through intramolecular ring-closure, and the catalyst was regenerated.

Reaction with 2-aminobenzonitriles

According to the possible mechanism mentioned above, the H atom and the basic [BO$_2$]$^-$ from the IL **[DBUH][BO$_2$]** were the key factors that influenced its catalytic activity. Coincidentally, for the reactions of CO$_2$ and 2-aminobenzonitriles into quinazoline-2,4(1*H*,3*H*)-diones, the strong basicity that could activate the amino group of 2-aminobenzonitriles was necessary for the catalyst,[27] while the IL **[DBUH][BO$_2$]** met this condition. Therefore, in order to verify indirectly the mechanism which we proposed, and broaden the application range of the IL **[DBUH][BO$_2$]**, the reaction of CO$_2$ with 2-aminobenzonitrile to quinazoline-2,4-(1*H*,3*H*)-dione catalyzed by **[DBUH][BO$_2$]** was conducted at 0.1 MPa CO$_2$ and room temperature, and the results are shown in Scheme 4. To our delight, the IL **[DBUH][BO$_2$]** showed good catalytic activity for this reaction,

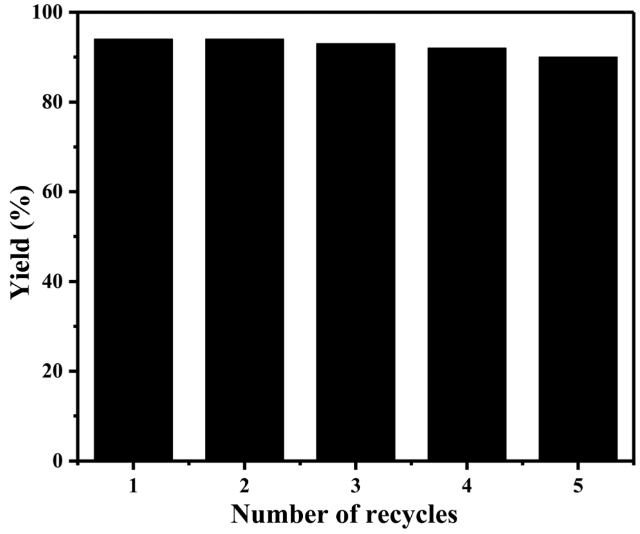
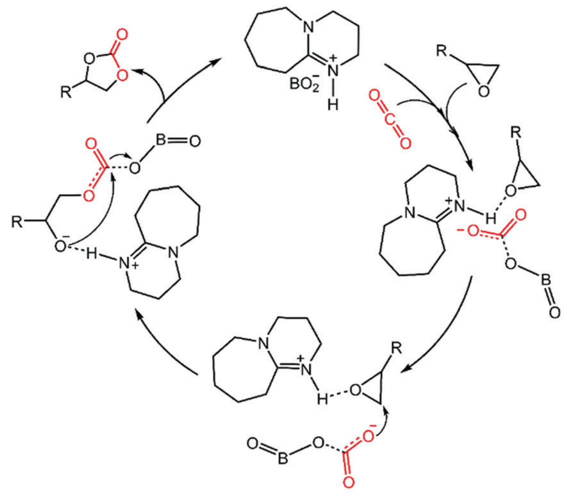
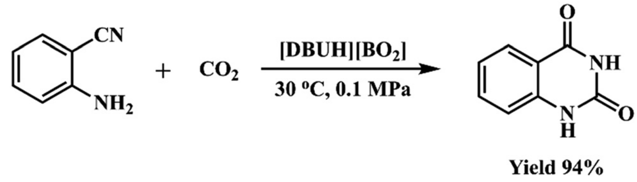


Fig. 3 Recyclability of **[DBUH][BO$_2$]**. Reaction conditions: **1a** (2 mmol, 0.1850 g), IL (1.5 mmol, 0.2941 g), CO$_2$ (0.1 MPa), 30 °C and 6 h.



Scheme 3 Proposed mechanism for the **[DBUH][BO$_2$]** catalyzed cycloaddition of epoxides and CO$_2$.



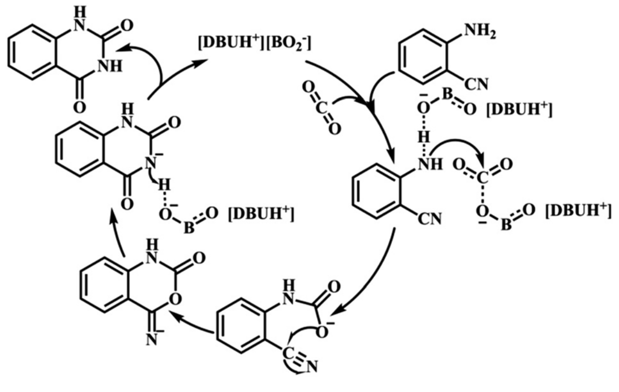
Scheme 4 The reaction of CO_2 and 2-aminobenzonitrile into quinazoline-2,4(1*H*,3*H*)-dione catalyzed by **[DBUH][BO2]**.

and the isolated yield of the target product quinazoline-2,4-(1*H*,3*H*)-dione was up to 94% in 6 h.

In addition, on the basis of the related knowledge in the literature,[29,30] a possible mechanism for the IL **[DBUH][BO2]** catalyzed reaction of CO_2 and 2-aminobenzonitriles is shown in Scheme 5. Firstly, the $[BO_2]^-$ with strong basicity could attack both the H atom of the amino group of 2-aminobenzonitrile and the C atom of CO_2. In this way, the electrophilic attack of CO_2 on the amino group is more favorable, and the carbamate anion, as well as HBO_2, was formed. Then, intramolecular nucleophilic cyclization and subsequently a rearrangement occur to form a quinazoline anion. Finally, the quinazoline anion extracts the proton from HBO_2 to form the target product, and the basic IL can be recovered for the second cycle.

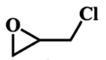
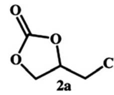
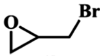
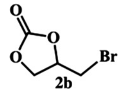
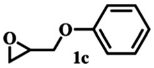
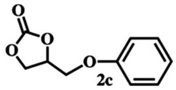
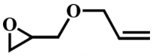
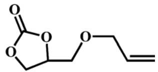
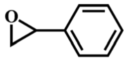
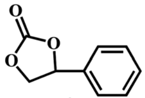
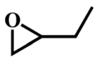
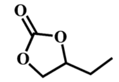
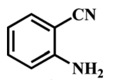
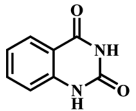
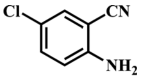
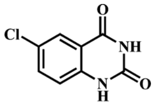
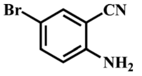
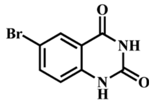
Catalyst generality

Finally, in order to explore the universality of the IL **[DBUH][BO2]**, the reactions of CO_2 with different substituted epoxides and with different substituted 2-aminobenzonitriles were examined using **[DBUH][BO2]** as the catalyst under mild conditions and the isolated yields of the target products are summarized in Table 2. For the reactions of CO_2 with different substituted epoxides, the reactivity of the epoxides depended strongly on the size of the substituted R group instead of the electronic effects of the substituted R group. When R groups were Br (**2b**, **2e**, electron-withdrawing group) and the alkoxy group (**2c**, **2d**, electron-donating group) that were bigger than Cl, the reactions could require a long time or even higher reaction temperature to complete (Table 2, entries 2–5). But when R was a methyl group, the desired product **2f** was not detectable. For the reactions of CO_2 with different substituted 2-aminobenzonitriles, the reactivity of the 2-aminobenzonitriles also depended strongly on the substituted R group, and the reaction was sensitive to the electronic effect of substituted R. When R was a halogen with some electron-withdrawing effects, a much longer time was needed to complete the reaction (**2g**–**2i**).



Scheme 5 Proposed mechanism for the reaction of CO_2 and 2-aminobenzonitriles.

Table 2 Reactions of various substrates with CO_2 catalyzed by **[DBUH][BO2]**[a]

Entry	Substrate	Product	Reaction time (h)	Yield (%)
1	 **1a**	 **2a**	6	93
2	 **1b**	 **2b**	24	91 96[b]
3	 **1c**	 **2c**	72	90[b]
4	 **1d**	 **2d**	72	89[c]
5	 **1e**	 **2e**	72	67[c]
6	 **1f**	 **2f**	6	0
7	 **1g**	 **2g**	6	94[d]
8	 **1h**	 **2h**	12	88[d]
9	 **1i**	 **2i**	12	90[d]

[a] Reaction conditions: substrate 2 mmol, **[DBUH][BO2]** 1.5 mmol (0.2941 g), CO_2 0.1 MPa, 30 °C. [b] **[DBUH][BO2]** 0.5 mmol (0.0980 g). [c] The reaction temperature was 80 °C. [d] **[DBUH][BO2]** 6 mmol (1.1764 g), methylbenzene (1 mL).

Conclusions

In conclusion, **[DBUH][BO2]** was synthesized successfully and utilized as the catalyst to effectively promote the reactions of CO_2 and epoxides under solvent- and halogen-free conditions at atmospheric pressure and room temperature with high yields of cyclic carbonates. Compared with other halogen-free ILs, the IL **[DBUH][BO2]** can be prepared more easily and has better catalytic universality. Moreover, this IL could be easily recovered and reused at least five times without any obvious loss of activity. The basic anion and the cation with N–H had an excellent synergistic catalytic effect on promoting these reactions. In addition, this basic IL, the anion of which had a strong nucleophilic ability, could also catalyze the reactions of CO_2 and 2-aminobenzonitriles into quinazoline-2,4(1*H*,3*H*)-diones at atmospheric pressure and room temperature, giving the desired products in high yields. As far as we know, the IL **[DBUH][BO$_2$]** that had an excellent catalytic activity for the reactions of CO_2 and epoxides as well as those of CO_2 and 2-aminobenzonitriles was reported for the first time. We hope that this IL has more potential applications in CO_2-relevant reactions and will provide ideas for other IL-based catalysts.

Conflicts of interest

There are no conflicts to declare.

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