Heterocycles

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# A Protic Ionic Liquid Catalyzes $CO_2$ Conversion at Atmospheric Pressure and Room Temperature: Synthesis of Quinazoline-2,4-(1*H*,3*H*)-diones**

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***Abstract:*** *The chemical fixation of $CO_2$ under mild reaction conditions is of significance from a sustainable chemistry viewpoint. Herein a $CO_2$-reactive protic ionic liquid (PIL), [HDBU$^+$][TFE$^-$], was designed by neutralization of the superbase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with a weak proton donor trifluoroethanol (TFE). As a bifunctional catalyst for simultaneously activating $CO_2$ and the substrate, this PIL displayed excellent performance in catalyzing the reactions of $CO_2$ with 2-aminobenzonitriles at atmospheric pressure and room temperature, thus producing a series of quinazoline-2,4(1H,3H)-diones in excellent yields.*

Chemical conversion of $CO_2$ is an alternative for $CO_2$ utilization, and has been paid much attention in the past decades.[1] In comparison with toxic phosgene and CO, $CO_2$ is an abundant, easily available, environmentally friendly, and renewable C1 building block. However, $CO_2$ conversion is limited because of its inherent thermodynamic stability, thus resulting in low reactivity. In this context, the key issue to convert $CO_2$ into useful chemicals under mild reaction conditions will inevitably rely on its activation. Therefore, effective catalytic systems are highly required. So far, many efficient catalysts have been developed for $CO_2$ conversion into high-value chemicals such as methanol,[2] formic acid,[3] and others.[4] However, high temperature and pressure are generally needed. In recent years, researchers have paid much attention to chemically converting $CO_2$ under mild reaction conditions, especially at atmospheric pressure and room temperature.[5] Kimura et al. reported $[(n\text{-}C_4H_9)_4N]_2^+[WO_4]^{2-}$ as a bifunctional catalyst which could catalyse the reactions of $CO_2$ with various aromatic diamines at atmospheric pressure around 100 °C.[5g] More recently, cobalt-coordinated conjugated microporous polymers were reported to function as heterogeneous catalysts for the reaction of $CO_2$ with propylene oxide at atmospheric pressure and room temperature.[5h] Though much progress has been made, the chemical conversion of $CO_2$ at atmospheric pressure and room temperature is still a challenge.

Ionic liquids (ILs) composing of organic cations and inorganic/organic anions have unique features such as high thermal and chemical stability, negligible vapor pressure, easy recyclability, and tunable properties, which have been applied in many areas.[6] Specifically, task-specific ILs have displayed superior performance for $CO_2$ capture and conversion through careful design and choice of novel component ions to endow them with unique properties.[4c,d,h,7] For example, superbase-derived protic ionic liquids (PILs) were presented to be excellent media for rapid and reversible capture of $CO_2$ under mild reaction conditions.[7b] $CO_2$ could react with PILs to form liquid carbonate, carbamate, or phenolate salts, which might result in activation of $CO_2$, thus rendering the chemical transformation of $CO_2$ under mild reaction conditions. Inspired by this progress, we designed a $CO_2$-reactive PIL using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a superbase and trifluoroethanol (TFE) as a proton donor, denoted as [HDBU$^+$][TFE$^-$]. This PIL could adsorb $CO_2$ with maximum molar ratio $CO_2$/IL of 1.01 at atmospheric pressure and room temperature (see the Supporting Information), thus suggesting that it was a good absorbent for $CO_2$ with a capacity comparable to those reported PILs.[7b]

Quinazoline-2,4(1*H*,3*H*)-diones can serve as intermediates for the synthesis of pharmaceuticals.[8] The reaction of $CO_2$ with 2-aminobenzonitriles is an atom-economical route for the synthesis of these compounds, and it has been widely investigated using various catalysts including DBU,[9] $Cs_2CO_3$,[10] MgO-$ZrO_2$,[11] [Bmim]OH,[12] *N*-methyl-tetrahydropyrimidine,[13] guanidines,[14] $[(n\text{-}C_4H_9)_4N]_2^+[WO_4]^{2-}$,[5g,15] and 1-butyl-3-methylimidazolium acetate ([Bmim]Ac).[16] However, in these studies a high $CO_2$ pressure and temperature were generally required. In this work, we have found that by using [HDBU$^+$][TFE$^-$] as the catalyst and solvent, the $CO_2$ reaction with 2-aminobenzonitriles at atmospheric pressure and room temperature produces a series of quinazoline-2,4(1*H*,3*H*)-diones in excellent yields. Moreover, the IL could be easily recovered and reused without activity loss.

[HDBU$^+$][TFE$^-$] was synthesized by neutralization of DBU and TFE, as illustrated in Scheme 1. The characterization for this IL is given in the Supporting Information, and the $^1$H NMR data (Figure S1) and FTIR (Figure S2) analysis confirm its formation. For comparison, other three ILs with different cations and anions, including, [HDBU$^+$][$CH_3COO^-$], [HTMG$^+$][TFE$^-$], and [Et-DBU$^+$][TFE$^-$]

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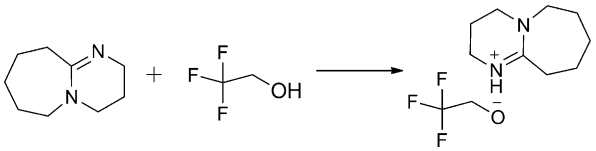


***Scheme 1.*** Preparation of [HDBU$^+$][TFE$^-$].

***Table 1:*** Reaction of 2-aminobenzonitrile with $CO_2$ catalyzed by different IL catalysts.[a]

| Entry | Catalyst/Solvent | Yield [%][b] |
|---|---|---|
| 1 | – | 0 |
| 2 | [HDBU$^+$][TFE$^-$] | 97 |
| 3 | [HDBU$^+$][$CH_3COO^-$] | 15 |
| 4 | [HTMG$^+$][TFE$^-$] | 67 |
| 5 | [Et-DBU$^+$] [TFE$^-$] | 7[c] |
| 6[d] | $[(n\text{-}C_4H_9)_4N]_2^+$ $[WO_4]^{2-}$ | 90 |

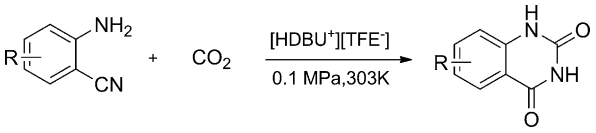
[a] Reaction conditions: 2-aminobenzonitrile (1 mmol), catalyst (3 mmol), $CO_2$ (0.1 MPa), 303 K, 24 h. [b] Yield of isolated product. [c] determined by LC analysis. [d] DMSO (1 mL), catalyst (0.02 mmol), $CO_2$ (0.1 MPa), 373 K, 120 h.[5g]

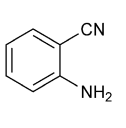
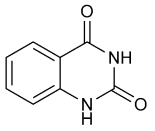
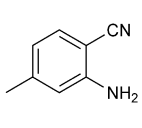
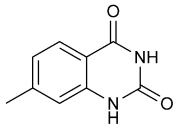
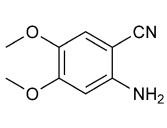
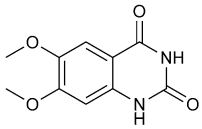
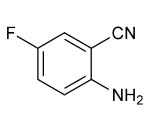
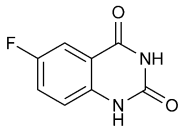
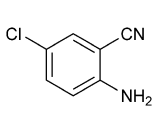
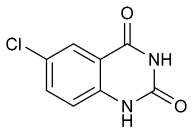
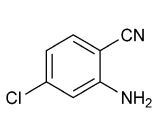
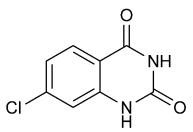
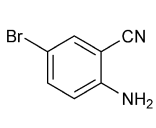
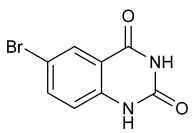
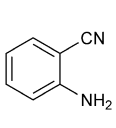
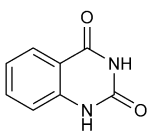
(TMG = 1,1,3,3-tetramethylguanidine), were synthesized (see the Supporting Information).

The reaction of $CO_2$ with 2-aminobenzonitrile was carried out in the absence and presence of the as-synthesized ILs, and the results are listed in Table 1. This reaction did not proceed in the absence of any catalyst. To our delight, [HDBU$^+$][TFE$^-$] as the catalyst showed high efficiency for this reaction (see Figures S3 and S4 in the Supporting Information), thus producing quinazoline-2,4(1*H*,3*H*)-dione in 97% yield, without any byproducts, within 24 hours (Table 1, entry 2). Moreover, [HDBU$^+$][TFE$^-$] served as a solvent, which allowed the reaction to proceed more rapidly than the reported systems.[5g] For comparison, three other ILs were examined for catalyzing this reaction. It was indicated that they were also effective, however, they showed lower activities (Table 1, entries 3–5). The differences in their chemical structures may be responsible for their activities. [HDBU$^+$][$CH_3COO^-$], having the same cation as [HDBU$^+$][TFE$^-$], afforded a much lower product yield (15%), thus indicating that the anions of the PILs influence the activities of the catalysts. Additionally, [HTMG$^+$][TFE$^-$] and [Et-DBU$^+$][TFE$^-$], which have the same anion as [HDBU$^+$][TFE$^-$], also gave lower product yields (67 and 7%, respectively), thus suggesting that the cations of the ILs affected the activities of the catalysts as well. From the above findings, it can be inferred that both the cations and anions of these ILs played important role in the reaction.

The [HDBU$^+$][TFE$^-$]-catalyzed system could be applied to various 2-aminobenzonitriles reacting with $CO_2$ at atmospheric pressure and room temperature (Table 2). It was demonstrated that all reactions proceeded smoothly, thus producing the corresponding quinazoline-2,4(1*H*,3*H*)-diones. With the exception of 4-methyl-2-aminobenzonitrile (Table 2, entry 2), the other 2-aminobenzonitriles, having substituents including methoxy, fluoro, chloro, and bromo groups, generated the corresponding products in excellent yields within

***Table 2:*** Synthesis of various quinazoline-2,4 (1*H*,3*H*)-diones.[a]



| Entry | Substrate | Product | Yield [%][b] |
|---|---|---|---|
| 1[c] |  |  | 97 |
| 2 |  |  | 68[d] |
| 3 |  |  | 92 |
| 4 |  |  | 96[d] |
| 5 |  |  | 92 |
| 6 |  |  | 90 |
| 7 |  |  | 95 |
| 8[e] |  |  | 95 |

[a] Reaction conditions: Reactant (1 mmol), [HDBU$^+$][TFE$^-$] (6 mmol), $CO_2$ (0.1 MPa), 303 K, 24 h. [b] Yield of isolated product. [c] [HDBU$^+$][TFE$^-$] (3 mmol). [d] Determined by LC analysis. [e] [HDBU$^+$][TFE$^-$] used for the fifth time.

24 hours. For example, 2-amino-4,5-dimethoxybenzonitrile afforded a 96% yield of 6,7-dimethoxyquinazoline-2,4-(1*H*,3*H*)-dione (Table 2, entry 3), which is a key intermediate in the synthesis of Prazosin, IAAP, and Doxazosin.[8b] The above results indicate that the substituents in the phenyl ring of 2-aminobenzonitriles have little effect on the reactivity with $CO_2$, and [HDBU$^+$][TFE$^-$] was highly efficient for catalyzing these reactions.

In addition, the reusability of [HDBU$^+$][TFE$^-$] was evaluated for the synthesis of quinazoline-2,4(1*H*,3*H*)-dione

from $CO_2$ and 2-aminobenzonitrile. It was demonstrated that the product yield almost remained unchanged as the same IL was used for five reactions (Table 2, entry 8), thus suggesting the designed IL maintained its original performance and was recyclable.

To explore the reaction mechanism, the interactions of [HDBU$^+$][TFE$^-$] with $CO_2$ and substrate were examined by NMR spectroscopy and IR analysis. The absorption of $CO_2$ by [HDBU$^+$][TFE$^-$] was examined by FTIR and NMR analyses. In the $^{13}$C NMR spectrum, a new signal appeared at $\delta =$ 167.7 ppm (Figure 1), which was attributed to the carbonyl

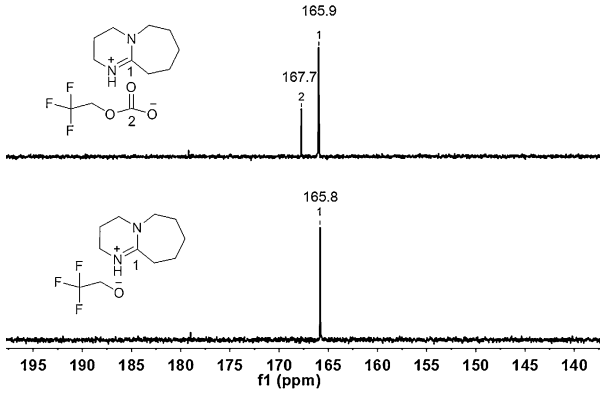



***Figure 1.*** $^{13}$C NMR spectrum of pure [HDBU$^+$][TFE$^-$] and the intermediate derived from exposure of [HDBU$^+$][TFE$^-$] to $CO_2$ (0.1 MPa; $D_2O$, 0.6 mL, 298 K).

carbon atom of the carbonate and suggests that $CO_2$ was activated by the anion [TFE$^-$], thus forming a carbonate intermediate. This intermediate in agreement with those previously reported.[7b] In our previous work we found that [HDBU$^+$] could activate $CO_2$ at 9 MPa and thus had a $^{13}$C NMR signal at $\delta = 172.3$ ppm,[4h] however, in this work the absence of this signal implies that at atmospheric pressure [HDBU$^+$] could not activate $CO_2$. In the FTIR spectrum a new band appeared at 1702 cm$^{-1}$ (see Figure S5 in the Supporting Information), which is assigned to the stretching vibration of the C=O bond of carbonate, thus confirming the formation of carbonate and the $^{13}$C NMR data. This carbonate may be the key intermediate for the $CO_2$ conversion.

The $^1$H, $^{13}$C, and $^{15}$N NMR analyses for [HDBU$^+$][TFE$^-$], 2-aminobenzonitrile, and their mixture were carried out. The $^1$H NMR signal of the $NH_2$ of 2-aminobenzonitrile in the mixture shifted from $\delta = 5.98$ (the shift of $NH_2$ in pure 2-aminobenzonitrile) to 6.03 ppm, and showed broadening (see Figure S6 in the Supporting Information), thus suggesting the hydrogen bonding between the IL and the substrate. In contrast, all the $^{15}$N NMR signals assigned to the N atoms of the IL and 2-aminobenzonitrile shifted accordingly upon the mixing these two compounds (Figure 2). Specifically, the $^{15}$N NMR signals for $NH_2$ of 2-aminobenzonitrile and for NH of [HDBU$^+$] shifted significantly, thus indicating the hydrogen bonding between [HDBU$^+$] and the substrate. Considering that [Et-DBU$^+$][TFE$^-$] afforded a much lower yield of quinazoline-2,4(1*H*,3*H*)-dione as compared with [HDBU$^+$][TFE$^-$] (Table 1, entries 2 and 5), it can be deduced that the

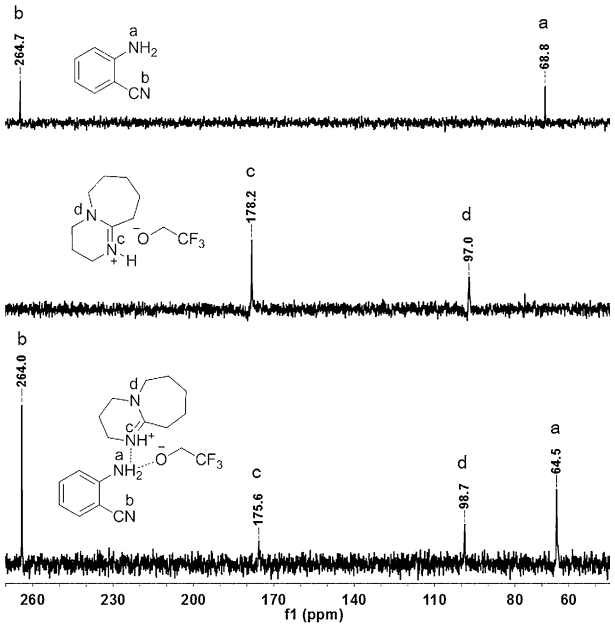
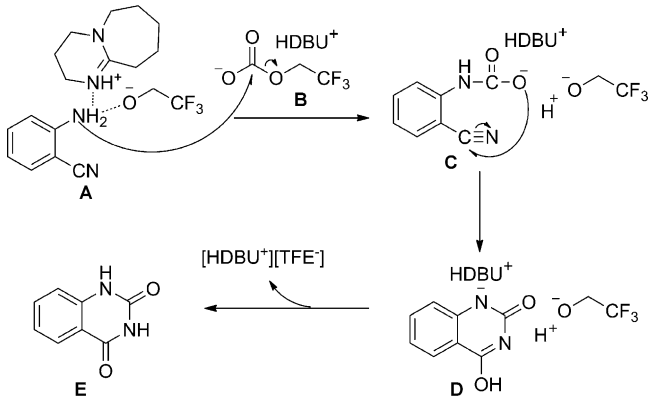



***Figure 2.*** $^{15}$N NMR spectrum of [HDBU$^+$][TFE$^-$] and 2-aminobenzonitrile, with and without [HDBU$^+$][TFE$^-$] ([D$_6$]DMSO, 298 K).

hydrogen bonding between [HDBU$^+$] and the substrate was very important for the synthesis of quinazoline-2,4(1*H*,3*H*)-dione from $CO_2$ reacting with 2-aminobenzonitrile. In addition, the $^{13}$C NMR signal, assigned to C1 in [TFE$^-$], shifted downfield from $\delta = 58.94$ to 58.98 ppm as the IL was mixed with 2-aminobenzonitrile (see Figure S7 in the Supporting Information), further indicating the formation of hydrogen bonding between [TFE$^-$] and the substrate. The above results indicated that both the cation and anion of the IL could form hydrogen bonds with the substrate, and could weaken the N–H bond in $NH_2$ of 2-aminobenzonitrile, thus facilitating the nucleophilic attack of the $NH_2$ group in 2-aminobenzonitrile on the carbon atom of the activated $CO_2$. From the above analysis, it can be deduced that the IL can serve as a bifunctional catalyst for simultaneously activating $CO_2$ and the substrate at atmospheric pressure and room temperature.

On the basis of the experimental results and previous reports,[5g,9–16] a possible mechanism for the [HDBU$^+$][TFE$^-$]-catalyzed reaction of $CO_2$ with 2-aminobenzonitrile to give quinazoline-2,4(1*H*,3*H*)-dione (**E**) is proposed (Scheme 2). In [HDBU$^+$][TFE$^-$], 2-aminobenzonitrile is activated by hydrogen bonding with both the cation and anion of the IL to form the intermediate **A**, while $CO_2$ is activated by the anion [TFE$^-$] to form the intermediate **B**. The nucleophilic nitrogen atom of **A** attacks the carbon atom of **B** to form the intermediate **C**, with subsequent nucleophilic cyclization of **C** to produced **D**, which is subsequently converted into **E** after regeneration of [HDBU$^+$][TFE$^-$].

In summary, a bifunctional IL catalyst, [HDBU$^+$][TFE$^-$], was designed by neutralization of a superbase (DBU) and a weak proton donor (trifluoroethanol), and found to activate $CO_2$ and 2-aminobenzonitriles simultaneously to produce quinazoline-2,4(1*H*,3*H*)-diones in excellent yields under atmospheric pressure at room temperature. In addition, this




***Scheme 2.*** Possible reaction pathway.

IL could be easily recovered and reused without loss in its activity. We believe that this kind of highly efficient, greener, and stable bifunctional IL catalytic system is promising for chemical fixation of $CO_2$ and generation of various useful chemicals under mild reaction conditions.

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**Keywords:** carbon dioxide fixation · heterocylces · ionic liquids · reaction mechanism · synthetic methods

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