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DBU-Based Ionic-Liquid-Catalyzed Carbonylation of *o*-Phenylenediamines with CO_2 to 2-Benzimidazolones under Solvent-Free Conditions

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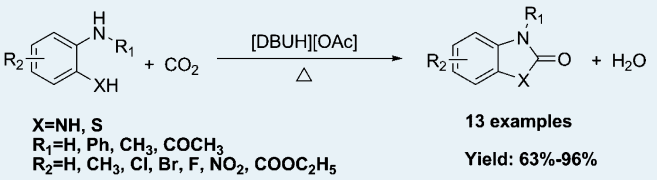
Supporting Information

ABSTRACT: Herein, a new route was presented to synthesize 2-benzimidazolones via the carbonylation of *o*-phenylenediamines with CO_2 catalyzed by 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)-based ionic liquids under solvent-free conditions. DBU acetate ([DBUH][OAc]) displayed high efficiency for catalyzing the reactions of CO_2 with *o*-phenylenediamines, and a series of benzimidazolones were obtained in high yields. It was demonstrated that [DBUH][OAc] could serve as a bifunctional catalyst for these reactions with the cation activating CO_2 and the anion activating *o*-phenylenediamines. This protocol provides an effective and environmentally friendly alternative route for production of benzimidazolones, and extends the chemical utilization of CO_2 in organic synthesis as well.



KEYWORDS: *carbon dioxide, ionic liquid, catalysis, carbonylation, benzimidazolone*

1. INTRODUCTION

Benzimidazolones are important derivatives of benzimidazoles found to exhibit a wide range of biological activities,[1−3] and the heterocyclic compounds incorporating the benzimidazolone moiety have received considerable attention.[4−6] To date, many synthetic approaches have been developed for the synthesis of benzimidazolone and its derivatives. The conventional methods are based on phosgenation of *o*-phenylenediamine,[7] which are being gradually discarded since phosgene is highly toxic. Several nonphosgenen approaches have been reported recently, including reactions of *o*-phenylenediamines with urea,[8] dimethyl carbonate,[9] or carbon monoxide,[10] and reaction of 2-amino-benzamide with iodosylbenzene.[11] Although much progress has been made for the synthesis of benzimidazolones, most of the synthetic methods suffer from their inherent limitations, such as the use of harmful chemicals (e.g., carbon monoxide), involving volatile organic solvents, low product yields, requirements for excess of reagents or catalysts, etc. Consequently, developing environmentally benign approaches using the cheap and unharmful starting materials is highly desirable.

In recent years, the conversion of CO_2 into valuable chemicals has received increasing attention, because of its economical and nontoxic characteristics, potential as a renewable C1 resource, and a carbonyl reagent alternative to toxic phosgene and CO.[12,13] So far, CO_2 has been converted into some valuable chemicals, such as formic acid,[14] methanol,[15] ureas,[16] esters,[17] formamidine derivatives,[18] benzimidazoles,[19] etc. In particular, the chemical conversion of CO_2 into heterocycles, such as benzimidazoles, is of paramount importance from a standpoint of green chemistry and sustainable development. We recently reported a simple and efficient synthesis of benzimidazole from a reaction of CO_2 with *o*-phenylenediamine in the presence of H_2 catalyzed by homogeneous catalyst $Ru(Cl)_2(dppe)_2$ under solvent-free conditions.[19] It was noteworthy that a byproduct, 2-benzimidazolone was detected with a trace amount accompanied with benzimidazole, which may form only from the reaction of *o*-phenylenediamine with CO_2, excluding the H_2 involvement. To test this hypothesis, the reaction of *o*-phenylenediamine with CO_2 using organic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as catalyst was performed. Excitingly, benzimidazolone was proved to be the sole product in high yield. Compared to the traditional synthetic methods or the recent new routes, the synthesis of benzimidazolones utilizing CO_2 as a feedstock is more attractive from the green and sustainable chemistry viewpoint. In preparation of this work, a bifunctional tungstate catalyst for chemical fixation of CO_2 was reported to produce various useful chemicals, including benzimidazolones.[20] Though significant progress has been made, developing a highly efficient, environmentally benign, thermally stable, recyclable catalyst for the synthesis of benzimidazolones from CO_2 and *o*-phenylenediamines is still desirable.

Room-temperature ionic liquids (ILs) have currently attracted significant attention due to their distinctive properties,

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such as negligible vapor pressure, high thermal stability, wide liquid temperature range, easy recyclability, excellent chemical stability, and strong solvent power for a wide range of organic and inorganic molecules. By modification of cations and/or anions, the properties of ILs can be turned in many ways. To date, a great number of functional ILs have been designed for different purposes.[21] Especially, they have been widely applied in organic synthesis as solvents or catalysts,[22−25] mainly including coupling reaction,[26] Michael addition,[27] Diels−Alder reaction,[28] Knoevenagel condensation,[29] Aldol reaction,[30] oxidation,[31] and reduction.[32]

DBU is a strong organic base and has been extensively applied in the base-induced reactions with excellent catalytic activity. However, the separation of DBU from the product mixture is generally difficult. The DBU-based ILs (DBU-ILs) overcome this drawback and exhibit the similar basicity to DBU accompanied with the general features of ILs. In this work, four DBU-ILs, including DBU acetate ([DBUH][OAc]), DBU lactate ([DBUH][Lac]), DBU chloride ([DBUH][Cl]),and *n*-butyl DBU acetate ([*n*-Bu-DBUH][OAc]), were synthesized, and their activity for catalyzing the carbonylation of *o*-phenylenediamine with CO_2 under solvent-free conditions was investigated. In addition, a series of benzimidazole derivatives were synthesized via the reactions of CO_2 with *o*-phenylenediamine catalyzed by [DBUH][OAc]. The possible reaction mechanism was discussed as well.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. CO_2 (99.99%) was provided by Beijing Analytical Instrument Company. DBU (99%), *o*-phenylenediamine (**1a**: 98%), 3,4-diaminotoluene (**1b**: 97%), 4,5-dimethyl-*o*-phenylene diamine (**1c**: 98%), 4-chloro-*o*-phenylenediamine (**1d**: 97%), 4-bromo-*o*-phenylenediamine (**1e**: 97%), 4-fluoro-*o*-phenylene diamine (**1f**: 97%), 4-trifluoromethyl-*o*-phenylenediamine (**1g**: 98%), 4-nitro-*o*-phenylenediamine (**1h**: 98%), ethyl-3,4-diaminobenzoate (**1i**: 97%), 3,4-diaminobenzophenone (**1j**: 97%), *n*-phenyl-*o*-phenylenediamine (**1k**: 98%), *N*-methyl-1,2-phenylenediamine (**1l**: 98%), 2′-aminoacetanilide (**1m**: 98%), and 2-aminothiophenol (**1o**: 97%) were purchased from Alfa Aesar and used without further purification. *N*,*N*′-Dimethy-1,2-phenylenediamine (**1n**) was prepared from *o*-phenyldiamine in two steps.[33]

TLC analysis was performed on silica gel 60 F_{254}, and the spots were visualized with UV light at 254 nm or under iodine. ^1H and ^{13}C NMR spectra were collected in $CDCl_3$ or $(CD_3)_2SO$ on a Bruker Avance NMR (400 MHz) at ambient temperature, and chemical shifts were recorded relative to tetramethylsilane (TMS). ^1H and ^{13}C NMR chemical shifts were reported in parts per million downfield from tetramethylsilane. The following abbreviations were used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2.2. General Procedures for the Synthesis of DBU-Based ILs. [DBUH][OAc] was synthesized according to the reported procedures.[34] In a typical experiment, in a N_2 atmosphere, DBU (5 mmol) was loaded into a 50 mL two-neck flask cooled in an ice−water bath, and acetic acid (5 mmol) was then added dropwise to the flask with stirring. After the mixture was stirred at 50 °C for 24 h, a light yellow, viscous oily liquid was obtained. Dried at 80 °C for 24 h under vacuum, the resultant product was characterized by ^1H NMR, which was in good agreement with the reported spectra data of [DBUH][OAc]. Similarly, [DBU][Lac] and [DBUH][Cl] were prepared by the reactions of DBU with lactic acid and hydrochloric acid, respectively, based on the reported procedures.[35]

2.3. General Procedures for the Carbonylation of *o*-Phenylenediamines to Benzimidazolones. All reactions for the carbonylation of *o*-phenylenediamines to benzimidazolones were carried out in a Teflon-lined stainless steel reactor of 22 mL coupled with a magnetic stirrer. In a typical experiment to synthesize benzimidazolone, *o*-phenylenediamine (2.0 mmol) and IL as the catalyst with the desired amount (e.g., [DBUH][OAc], 0.2 mmol) were loaded into the reactor, and moved subsequently to an oil bath at 120 °C, which was controlled by a Haake-D3 temperature controller. CO_2 was then charged into the reactor up to the desired pressure (e.g., 9 MPa), and the stirrer was started. After the reaction, the reactor was cooled in ice−water and the gas inside was slowly vented. The reaction mixture was extracted with ethyl acetate three times to separate the IL from the product. The combined solution of ethyl acetate was dried with Na_2SO_4 and then concentrated through vacuum evaporation to give the crude product, which was further purified by column chromatography. The recovered IL (e.g., [DBUH][OAc]) was dried in vacuo at 60 °C for 8 h and reused in the next reaction as the catalyst.

Similarly, the other benzimidazolone derivatives were synthesized via the reactions of CO_2 with the corresponding substituted *o*-phenylenediamines catalyzed by [DBUH][OAc].

2.4. NMR Spectra Data of the Synthesized Benzimidazolone Derivatives. ***2A**: 2-Benzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.241 g, 90%). The characterization data obtained for 2-benzimidazolone were identical to those previously reported in the literature.[36] ^1H NMR (400 MHz, DMSO-d_6, 293 K): δ 10.49 (s, 2H), 6.81 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ 155.7 (C), 130.1 (C), 120.8 (CH), 108.9 (CH).

***2B**: 5-Methylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.281 g, 95%). The characterization data obtained for 5-methylbenzimidazolone were identical to those previously reported in the literature.[36] ^1H NMR (400 MHz, DMSO-d_6): δ 10.41 (s, 1H), 10.37 (s, 1H), 6.66 (d, J = 7.7 Hz, 1H), 6.59 (d, J = 10.4 Hz, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.92 (CO), 130.34 (C), 129.76 (C), 127.93 (C), 121.30 (CH), 109.45 (CH), 108.60 (CH), 21.47 (CH_3).

***2C**: 4,5-Dimethylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.311 g, 96%). The characterization data obtained for 5,6-dimethylbenzimidazolone were identical to those previously reported in the literature.[37] ^1H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 2H), 6.71 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 155.96 (CO), 141.41 (C), 129.63 (C), 128.25 (CH), 20.34 (CH_3).

***2D**: 5-Chlorobenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.258 g, 77%). The characterization data obtained for 5-chlorobenzimidazolone were identical to those previously reported in the literature.[36] ^1H NMR (400 MHz, DMSO-d_6): δ 10.65 (s, 2H), 6.87−6.83 (m, 2H), 6.81 (s, 1H). ^{13}C NMR

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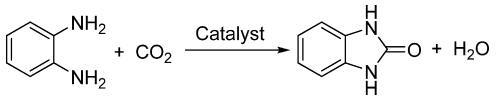
Table 1. Carbonylation of *o*-Phenylenediamine to Benzimidazolone with CO_2[a]



entry	catalyst	amount (equiv)	P_{CO_2} (MPa)	time (h)	yield[b] (%)
1	none	0	9	12	NR[c]
2	[DBUH][OAc]	1	9	24	97
3	[DBUH][Lac]	1	9	24	91
4	[*n*-BuDBU][OAc]	1	9	24	25
5	[DBUH][Cl]	1	9	30	NR[c]
6	[DBUH][OAc]	0.1	9	24	90[d],89[e],89[f],90[g],89[h]
7	[DBUH][OAc]	0.1	9	40	96
8	[DBUH][OAc]	0.1	6	24	81
9	[DBUH][OAc]	0.1	3	24	70
10	[DBUH][OAc]	0.1	1	24	51
11	[DBUH][OAc]	0.05	9	24	71
12	[DBUH][OAc]	0.01	9	24	47

[a]All reactions were carried out with *o*-phenylenediamine (2 mmol), 120 °C. [b]Yields of isolated product. [c]No reaction. [d]Yield of product (runs: 1). [e]Runs: 2. [f]Runs: 3. [g]Runs: 4. [h]Runs: 5.

(101 MHz, DMSO-d_6): δ 155.69 (CO), 131.32 (C), 129.10 (C), 124.94 (C), 120.56 (CH), 109.98 (CH), 108.84 (CH).

2E: *5-Bromobenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.302 g, 71%). The characterization data obtained for 5-bromobenzimidazolone were identical to those previously reported in the literature.[38] ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 2H), 7.07 (dd, J = 8.2, 1.9 Hz, 1H), 7.05 (s, 1H), 6.87 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 155.51 (CO), 131.68 (C), 129.46 (C), 123.37 (C), 112.47 (CH), 111.50 (CH), 110.54 (CH). HRMS calcd for $C_7H_5BrN_2O$: 213.0314. Found: 213.0311.

2F: *5-Fluorobenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.258 g, 85%). The characterization data obtained for 5-fluorobenzimidazolone were identical to those previously reported in the literature.[36] ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.74 (s, 1H), 10.62 (s, 1H), 6.87 (dd, J = 8.4, 4.7 Hz, 1H), 6.79−6.69 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 156.12 (CO), 130.86 (C), 130.74 (C), 126.51 (C), 109.24 (CH), 109.14 (CH), 107.06 (CH).

2G: *5-Trifluoromethylbenzimidazolone,.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.283 g, 70%). The characterization data obtained for 5-trifluoromethylbenzimidazolone were identical to those previously reported in the literature.[39] ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.02 (2H, s), 7.27 (d, J = 8.0 Hz, 1H), 7.16 (1 H, s), 7.09 (d, J = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 157.57 (CO), 132.37 (C), 129.36 (C), 125.71 (C), 123.01 (CF_3), 120.75 (CH), 120.43 (CH), 117.37 (CH).

2H: *5-Nitrobenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.247 g, 69%). The characterization data obtained for 5-nitrobenzimidazolone were identical to those previously reported in the literature.[36] ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.23 (s, 2H), 7.86 (dd, J = 8.7, 2.2 Hz, 1H), 7.65 (d, J = 2.2 Hz, 1H), 7.03 (d, J = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 157.77 (CO), 155.14 (C), 140.87 (C), 135.30 (C), 129.32 (CH), 117.35 (CH), 107.65 (CH).

2I: *5-Ethoxycarbonylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.313 g, 76%). Melting point: 135−136 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.04 (s, 1H), 10.86 (s, 1H), 7.63 (dd, J = 8.2, 1.3 Hz, 1H), 7.47 (s, 1H), 7.01 (d, J = 8.2 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.35 (CO), 155.86 (CO), 134.35 (C), 130.03 (C), 123.30 (C), 122.48 (CH), 109.40 (CH), 108.59 (CH), 60.79 (CH_2), 14.68 (CH_3). FTIR (KBr): 3089, 2983, 2801,1710, 1624, 1582, 1520,1475, 1414, 1367, 1305, 1232, 1123, 956, 892, 887,776,753 cm^{-1}. HRMS calcd for $C_{10}H_{10}N_2O_3$: 206.1980. Found: 206.1982.

2J: *5-Benzoylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.347 g, 73%). The characterization data obtained for 5-benzoylbenzimidazole were identical to those previously reported in the literature.[36] ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.10 (s, 1H), 10.87 (s, 1H), 7.74−7.60 (m, 3H), 7.54 (t, J = 7.5 Hz, 2H), 7.42 (dd, J = 8.2, 1.6 Hz, 1H), 7.32 (d, J = 1.4 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 194.65 (CO), 156.79 (CO), 137.97 (C), 135.90 (C), 131.15 (C), 130.24 (C), 128.63 (CH), 128.04 (CH), 127.79 (CH), 123.63 (CH), 109.07 (CH), 107.83 (CH).

2K: *N-Phenylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.336 g, 80%). The characterization data obtained for *N*-phenylbenzimidazole were identical to those previously reported in the literature.[11] ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.15 (s, 1H), 7.62−7.51 (m, 4H), 7.46−7.40 (m, 1H), 7.10−7.04 (m, 2H), 7.04−6.97 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 153.68 (CO), 135.04 (C), 130.46 (C), 129.86 (C), 128.91 (CH), 127.77 (CH), 126.37 (CH), 122.26 (CH), 121.35 (CH), 109.63 (CH), 108.57 (CH).

2L: *N-Methylbenzimidazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product

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(0.255 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.62 (s, 1H), 7.10−6.92 (m, 4H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.95 (CO), 130.93 (C), 128.17 (C), 121.51 (CH), 121.14 (CH), 109.63(CH), 107.53 (CH), 26.76 (CH_3). HRMS calcd for $C_8H_8N_2O$: 148.0637. Found: 148.0643.

2M: *2-Methyl-1H-benzimidazole.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.258 g, 98%). The characterization data obtained for benzimidazole were identical to those previously reported in the literature.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.55−7.57 (dd, 2H), 7.26−7.21 (dd, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.31 (CO), 137.63 (C), 121.12 (CH), 113.45 (CH), 13.90 (CH_3).

2O: *2-Benzothiazolone.* This compound was prepared according to the general procedure and was subjected to column chromatography on silica gel to afford the product (0.095 g, 63%). The characterization data obtained for benzimidazole were identical to those previously reported in the literature.[40] ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.87 (s, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.10 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 170.48 (CO), 136.79 (C), 126.82 (C), 123.77 (CH), 123.10 (CH), 123.02 (CH), 111.93 (CH).

3. RESULTS AND DISCUSSION

In this work, four DBU-ILs, including [DBUH][OAc], [DBUH][Lac], [DBUH][Cl], and [*n*-Bu-DBUH][OAc], were first synthesized, and they were used to catalyze the reaction of CO_2 with *o*-phenylenediamine. At the reaction temperature of 120 °C, *o*-phenylenediamine was in the liquid state and miscible with all the DBU-ILs. The reaction of CO_2 with *o*-phenylenediamine was performed in a two-phase reaction system under the experimental conditions as listed in Table 1. This reaction did not occur in the absence of any IL (Table 1, entry 1), whereas the presence of an IL, including [DBUH][OAc], [DBUH][Lac], and [*n*-BuDBU][OAc], in the reaction system, respectively, resulted in the production of benzimidazolone (Table 1, entries 2−4). However, [DBUH][Cl] could not catalyze the reaction of CO_2 with *o*-phenylenediamine (Table 1, entry 5). As listed in Table 1, [DBUH][OAc], [DBUH][Lac], and [DBUH][Cl] showed the activities in the order: [DBUH][OAc] > [DBUH][Lac] > [DBUH][Cl], though they had the same cation $[DBUH]^+$. This suggests that the anions of the ILs had an impact on the activities of the ILs for catalyzing this reaction. [*n*-BuDBU][OAc] could catalyze this reaction; however, it displayed a much lower activity compared to [DBUH][OAc] (Table 1, entry 4). This implies that the cations of the ILs may be involved in catalyzing the reaction. From the above findings, it can be deduced that both the cation and the anion of the IL played important roles in catalyzing the reaction of CO_2 with *o*-phenylenediamine, which will be discussed in the following section.

Among the four ILs, [DBUH][OAc] exhibited the best performance for catalyzing the reaction of CO_2 with *o*-phenylenediamine. Therefore, it was selected as the catalyst to investigate the influences of catalyst amount, CO_2 pressure, and reaction time on the reaction. With the equal equivalent of IL, a product yield of 97% was obtained under the experimental conditions (Table 1, entry 2). When the IL amount was decreased to 0.1 equiv, the benzimidazolone yield just reduced to 90% (Table 1, entry 6), and a product yield of 96% was achieved when the reaction time was prolonged to 40 h (Table 1, entry 7). Moreover, the reaction still proceeded as the IL amount further decreased to 0.05 equiv, and even to 0.01 equiv (Table 1, entries 11, 12). This indicates that this IL was very effective in catalyzing the reaction of CO_2 with *o*-phenylenediamine.

The CO_2 pressure was found to considerably influence the product yields, which reduced from 90% to 51% as the pressure decreased from 9 to 1 MPa, as shown in Table 1 (Entries 6, 8−10). This should be related to the phase behavior of the reaction system. The reaction system included two phases, the CO_2-rich phase and the liquid phase mainly containing *o*-phenylenediamine and the IL, and the reaction occurred in the liquid phase. Decreasing the CO_2 pressure rendered less CO_2 to dissolve into the liquid phase, which was unfavorable to CO_2 contacting with diamine and the catalyst, leading to low product yield finally. From the above results, the optimal experimental conditions were chosen as follows: [DBUH][OAc] as the catalyst with an amount of 0.1 equiv of the substrate and a CO_2 pressure of 9 MPa.

The recyclability of the catalyst [DBUH][OAc] for the reaction was investigated, and the results are shown in Figure 1.

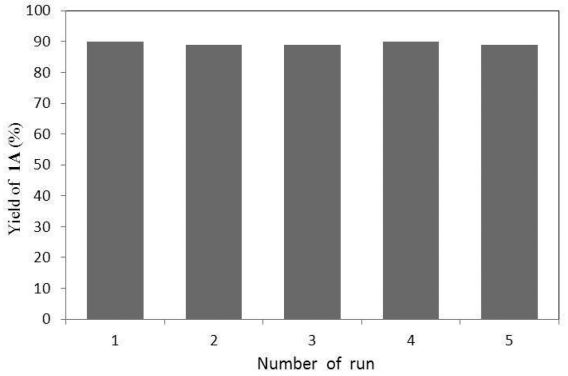

Figure 1. Yields of benzimidazolone (**1A**) obtained using the recycled [DBUH][OAc] as the catalyst.

It can be observed that the product yield almost stayed unchanged as the IL was reused five times, suggesting that the IL still retained its original activity. This indicates that the used IL was recyclable for catalyzing the reaction of CO_2 with *o*-phenylenediamine.

To broaden the scope and generality of the developed protocol, a wide range of substituted *o*-phenylenediamines were used to react with CO_2 under the optimal conditions, and the results are summarized in Table 2. It was demonstrated that all the substituted *o*-phenylenediamines bearing electron-donating and electron-withdrawing groups could react with CO_2 catalyzed by [DBUH][OAc], affording the corresponding benzimidazolone derivatives in moderate to high yields under the experimental conditions. Compared to *o*-phenylenediamine, the substituted *o*-phenylenediamines with electron-donating groups, for example, the Me group, produced the corresponding benzimidazolones with improved yields (Table 2, entries 2, 3), suggesting that the electron-donating groups made the *o*-phenylenediamines more active to react with CO_2. However, the *o*-phenylenediamines with electron-withdrawing groups from the weak electron-withdrawing groups, for example, F, Cl, and Br, to the strong electron-withdrawing groups, for example, CF_3, NO_2, CO_2Et, and PhCO, all generated the corresponding benzimidazolones in declined yields (Table 2, entries 4−10),

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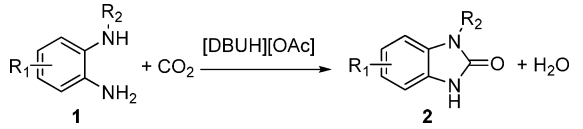
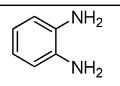
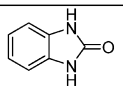
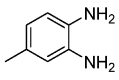
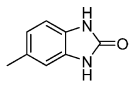
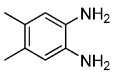
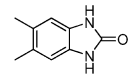
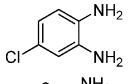
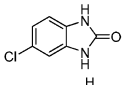
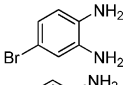
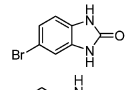
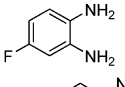
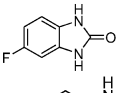
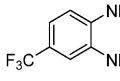
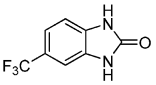
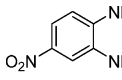
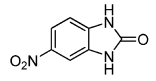
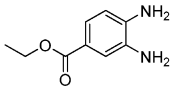
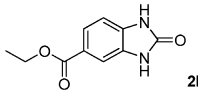
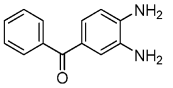
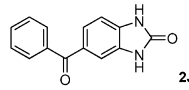
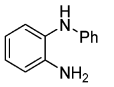
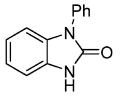
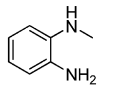
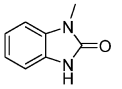
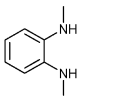
Table 2. Carbonylation of *o*-Phenylenediamines to Benzimidazolones Catalyzed by [DBUH][OAc][a,b,c]



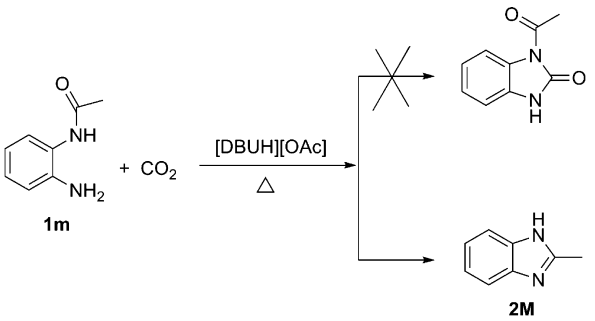
1 2

Entry	Substrate	Product	Yield/%[b]
1	 1a	 2A	90
2	 1b	 2B	95
3	 1c	 2C	96
4	 1d	 2D	77
5	 1e	 2E	71
6	 1f	 2F	85
7	 1g	 2G	70
8	 1h	 2H	69
9	 1i	 2I	76
10	 1j	 2J	73
11	 1k	 2K	80
12	 1l	 2L	86
13	 1n	—	NR[c]

[a]Reaction conditions: substrate, 2 mmol; [DBUH][OAc], 0.1 equiv; CO_2 pressure, 9 MPa; reaction temperature, 120 °C; reaction time, 24 h. [b]Isolated yield. [c]No reaction.

suggesting that the electron-withdrawing groups lowered the activity of the *o*-phenylenediamines reacting with CO_2. The above findings indicate that the substituents in the phenyl ring of diamines considerably influenced their activities to react with CO_2, and the *o*-phenylenediamines with electron-donating groups are more active than those with electron-withdrawing groups. The *o*-phenylenediamine with the N-substituent also generated the corresponding benzimidazolone in high yields (Table 2, entries 11 and 12), which indicates that the steric hindrance of the *N*-phenyl substituent seemed not to hamper the reaction. When 2′-aminoacetanilide (**1m**) was used as the diamine substrate under the similar conditions, the desired product (i.e., *N*-acetyl benzimidazolone) was not obtained. Instead, 2-methyl benzimidazole (**2M**) was obtained in a yield of 98%, which may be attributed to the cyclization of 2′-aminoacetanilide under the experimental conditions (Scheme 1). It is noteworthy that, when *N*,*N*′-dimethyl-*o*-phenylenediamine was used as the substrate, no product was formed, even though the reaction time was prolonged to 40 h (Table 2, entry 13), thus implying that the reaction may proceed via the isocyanate intermediate, which was consistent with that reported in the literature.[20]

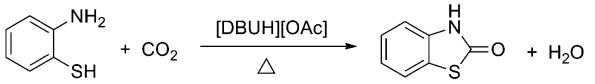
Scheme 1. Reaction of 2′-Aminoacetanilide with CO_2 Catalyzed by [DBUH][OAc]



1m 2M

2-Aminothiophenol was examined to react with CO_2 catalyzed by [DBUH][OAc]. Interestingly, benzothiazolone was successfully obtained with a yield of 63% (Scheme 2). This is the first example to produce benzothiazolone via the reaction of CO_2 with 2-aminothiophenol to the best of our knowledge, which may provide a new route to the production of 2-benzothiazolones.

Scheme 2. Synthesis of Benzothiazolone via 2-Aminothiophenol Reacting with CO_2[a]



1o 2O

[a]Reaction conditions: substrate, 1 mmol; [DBUH][OAc], 1 equiv; CO_2 pressure, 9 MPa; reaction temperature, 100 °C; reaction time, 24 h.

To better understand the reaction mechanism, NMR analysis was employed to identify the possible intermediates during the reaction. In the spectrum of the mixture of an equivalent of [DBUH][OAc] with *o*-phenylenediamine (Figure 2A), the signal assigned to the NH_2 proton of *o*-phenylenediamine shifted from δ = 4.34 to 4.52 ppm and the peak became wider, thus indicating the formation of a hydrogen-bonding interaction between [DBUH][OAc] and *o*-phenylenediamine. Moreover, in the corresponding ^{13}C NMR spectrum, the signal at δ = 178.6 ppm to the C1 atom of [DBUH][OAc] shifted to δ = 173.1 ppm upon mixing with *o*-phenylenediamine (Figure 2B), suggesting the stronger hydrogen-bonding interaction between $[OAc]^-$ and *o*-phenylenediamine. The hydrogen bond could weaken the N−H bond and facilitate the nucleophilic attack of the NH_2 group in *o*-phenylenediamine on the carbon atom of CO_2. In the spectrum of the intermediate of [DBUH][OAc] exposed to CO_2 (9 MPa), a new ^{13}C signal appeared at δ = 172.3 ppm (Figure 3), probably ascribed to the $[DBUH]^+/CO_2$ adduct, which was a key intermediate for accomplishing the reaction through activating CO_2 by the

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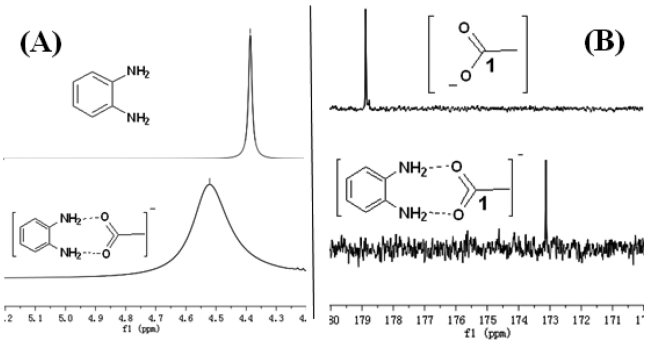


Figure 2. NMR spectra: (A) ^{1}H NMR of *o*-phenylenediamine (0.1 mmol) without and with [DBUH][OAc] (0.1 mmol), (DMSO-d_6, 0.6 mL, 298 K); (B) ^{13}C NMR of [DBUH][OAc] (0.1 mmol), without and with *o*-phenylenediamine (0.1 mmol), (DMSO-d_6, 0.6 mL, 298 K).

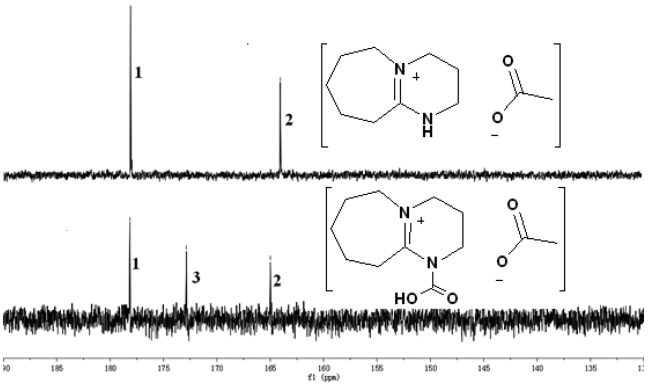
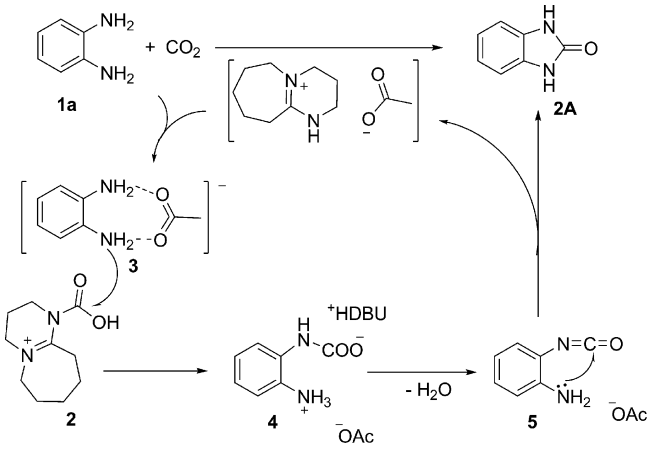


Figure 3. ^{13}C NMR spectra of pure [DBUH][OAc] (0.1 mmol) and the intermediate of [DBUH][OAc] exposed to CO_2 (9 MPa) (DMSO-d_6, 0.6 mL, 298 K).

tertiary nitrogen atom of the $[HDBU]^+$ cation. From the above results, it can be deduced that the cation of the IL activated CO_2 and the anion activated *o*-phenylenediamines, meaning that the IL acted as a bifunctional catalyst for the reaction of CO_2 with *o*-phenylenediamine. This can explain why [*n*-BuDBU][OAc] showed lower activity than [DBUH][OAc]. Because of the steric hindrance effect of its bulky cation, $[n\text{-BuDBU}]^+$ was incapable of activating CO_2, which led to a lower efficiency of [*n*-BuDBU][OAc] for catalyzing the reaction of CO_2 with *o*-phenylenediamine. In the case of [DBUH]Cl as the catalyst, Cl^- could not activate *o*-phenylenediamine, which may be responsible for the no activity for this reaction.

On the basis of the NMR experimental results and the previous report,[20,41] the possible reaction mechanism, similar to that proposed by Mizuno,[20] is shown in Scheme 3. We supposed that the reaction of CO_2 with *o*-phenylenediamine might undergo as follows. In the presence of [DBUH][OAc], CO_2 was activated by the tertiary N atom of $[DBUH]^+$ to form intermediate **2**; meanwhile, *o*-phenylenediamine (**1a**) was activated by hydrogen bonding with O atoms of the $[OAc]^-$ anion to form intermediate **3**. The nucleophilic nitrogen of intermediate **3** would attack the carbon atom of intermediate **2** to form intermediate carbamate **4**, followed by the dehydration of intermediate isocyanate **5**, which was not detected in our experiment, but could be deduced from the result of entry 12 in Table 2. Finally, the intramolecular nucleophilic attack of the

Scheme 3. The Possible Reaction Pathway



NH group on the carbon atom of isocyanate takes place to give the corresponding product **2A**.

4. CONCLUSION

The carbonylation of *o*-phenylenediamines with CO_2 was achieved using the DBU-based ILs as catalysts without any solvents and additives. [DBUH][OAc] displayed the best efficiency for the reactions of CO_2 with *o*-phenylenediamines, and a series of 2-benzimidazolones were synthesized in high yields. In these reactions, [DBUH][OAc] served as a bifunctional catalyst with the cation activating CO_2 and the anion activating *o*-phenylenediamines. This protocol to synthesize 2-benzimidazolones from CO_2 and *o*-phenylenediamine provides an effective and environmentally friendly alternative for production of benzimidazolones, and it also extends the chemical utilization of CO_2 in the synthesis of industrially important chemicals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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