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The simple system of fixing CO_2 to synthesize benzimidazolones at atmospheric pressure

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ABSTRACT

A simple chemical fixation of CO_2 at atmospheric pressure to make valuable benzimidazolones derivates via the *o*-phenylene-diamines carbonylation reaction catalyzed by DBU/S was developed. Different reaction conditions were examined and optimized. A series of benzimidazolones derivatives were synthesized using NMP as solvent at 413K with excellent yields (80–94%). Various substrates were employed and the results suggested the wide application of our method. The quantum mechanics calculations demonstrated that the complexation of DBU with sulfur significantly enhanced the reaction. This protocol rovides a novel approach of fixing CO_2 at atmospheric pressure into a series of 2-benzimidazolones derivates.

1. Introduction

Carbon dioxide, as an abundant, renewable and nontoxic C1 source, has received much attention in the past few years [1]. Efficient transformation of CO_2 into valuable organic chemicals at atmospheric pressure is an ideal approach which benefits the sustainable development of chemical industry and the sustainable low-carbon society. Researchers have made lots of fruitful exploration and many promising strategies for converting CO_2 to high value-added chemicals [2]. Chemical fixation of CO_2 by organic reactions is a promising approach. One of the key factors during the capturing process is to identify an efficient catalyst which can activate CO_2 in organic reactions. Many effective catalysts were developed, such as metal organic frameworks (MOFs), ionic liquids (ILs), organometallic reagents and so on [3]. Due to the low energy level of CO_2, large amount of energy are needed to activate it, transition metal catalysts are generally considered to be the most effective reagents [3]. Many reports employed relevant catalysts to convert CO_2 under high pressures. The transition metal catalysts are not only expensive but often demand complex preparation processes [4]. Therefore, developing suitable catalysts to fix CO_2 to synthesize valuable chemicals under mild reaction condition is very important and highly desirable.

Benzimidazolones are important intermediates for pharmaceuticals, and have been received considerable attention for their multi-biological activities [5–8]. Basically, benzimidazolone and its derivatives are synthesized by the reaction of diamines with reagents such as carbon monoxide [9], phosgene [10], urea [11], dimethyl carbonate (with 2-nitroaniline) [11c], and isocyanate [12]. However, these reagents are highly toxic or prepared from hazardous chemicals such as NH_3, CS_2 and so on. From the view of green chemistry, these hazardous chemicals should be replaced gradually. Thus, some catalyst systems, such as ([DBUH][OAc] [13] and $TBA_2[WO_4]$ [14]) were developed for capturing CO_2 in a greener way. However, these systems still require harsh reaction conditions such as high pressure (9 MPa), extended reaction time and the complex process of special catalysts preparation [13,14]. Consequently, developing simple and friendly approaches for preparing benzimidazolones by fixing CO_2 at atmospheric pressure is of high significance.

As part of our continuous efforts to develop a simple and efficient method to obtain the valuable heterocycles starting from CO_2 under atmospheric pressure [15], herein, we reported a simple and efficient method of fixing CO_2 to prepare benzimidazolones at 1atm (Scheme 1). It was discovered that the DBU/S system showed excellent catalytic ability for this fixation process.

2. Experimental

2.1. Materials

CO_2 was purchased from Hangzhou Special Gases Factory (99.99%). 1,8-diazabicyclo-[5.4.0]undec-7-ene(DBU,99%) was provided by Aladdin Chemistry Co. Ltd. *O*-phenylenediamines(1a–j) were obtained from Adamas Reagent Co. Ltd. or J & K Scientific Ltd. 2-Aminobenzenethiol(1k) was purchased from Tokyo Chemical Industry. Co. Ltd. The

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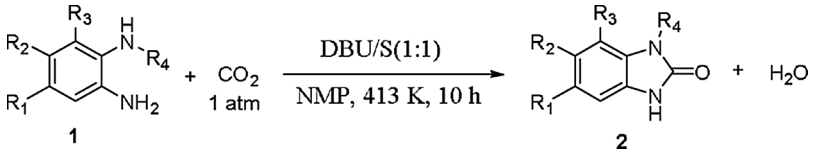

Scheme 1. Fixing CO_2 to synthesize benzimidazolones derivatives.

deuterated solvent (DMSO-d6) was purchased from J & K Scientific Ltd. All of the chemicals were used without further purification.

Nuclear magnetic resonance were carried out with a Bruker AV400 (500 MHz) with DMSO-d6 as the solvent using TMS as internal standard. Chemical shifts are expressed in ppm and coupling constants J are given in Hz.

2.2. General procedure

The general procedure is similar. As an example, the synthesis of compound 2a was carried out in a 20 mL glass tube (d = 2 cm) with a magnetic stirrer. In a typical experiment, *o*-phenylenediamine 1a (1 mmol), DBU (1 mmol), S (1 mmol) and NMP (1 mL) were added into the tube. CO_2 went into and bubbled through the tube, so the amount of CO_2 was in excess, and the CO_2 pressure was maintained at 1 atm. The tube was placed in a heating magnetic stirrer at the optimized temperature (413 K) and the reaction mixture was stirred. Thin-layer chromatography (TLC, petroleum ether / ethyl acetate, v/v, 10/1) was employed to track the completion of the reaction. Upon completion the tube was cooled down in ice − water bath, 10 mL water was added into it, and then the reaction mixture was extracted with ethyl acetate (5 × 10 mL). The combined solution of ethyl acetate was dried with anhydrous Na_2SO_4 and then concentrated by vacuum evaporation to afford the crude product, which was further purified by column chromatography (petroleum ether / ethyl acetate, v/v, 10/1). The residue of water was evaporated under vacuum at 50 °C for 8 h and reused in the next run. Taking the model reaction as an example, the product yield was still obtained at 78% on the third recycle (entry 27, Table 2). The products were characterized by ^{1}H NMR, ^{13}C NMR. Spectral characterizations of the products (2a–k) were obtained as follows, which were in accordance with the literatures.

2-Benzimidazolone (2a) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.55 (s, 2H), 6.92 (s, 4H), ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.72, 130.14, 120.84, 108.92.

5-Methylbenzimidazolone (2b) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.44 (d, *J* = 18.4 Hz, 2H), 6.80–6.72 (m, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.88, 130.32, 129.80, 127.92, 121.33, 109.46, 108.61, 21.46.

4-Methyl-2-benzimidazolone (2c) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.64 (s, 1H), 10.51 (s, 1H), 6.84–6.72 (m, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.96, 129.73, 129.05, 122.03, 120.81, 118.60, 106.52, 16.61.

4,5-Dimethylbenzimidazolone (2d) [13]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.32 (s, 2H), 6.70 (s, 2H), 2.18 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.90, 128.26, 128.22, 110.03, 19.86.

5-Fluorobenzimidazolone (2e) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.73 (s, 1H), 10.62 (s, 1H), 6.90–6.88 (m, 1H), 6.79–6.72 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.95 (d, *J* = 233.4 Hz), 156.14, 130.84 (d, *J* = 12.8 Hz), 126.53, 109.20 (d, *J* = 9.3 Hz), 106.94 (d, *J* = 24.0 Hz), 96.94 (d, *J* = 28.6 Hz).

5-Chlorobenzimidazolone (2f) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.74 (s, 2H), 6.96-6.90 (m, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 155.69, 131.33, 129.11, 124.97, 120.57, 109.98, 108.85.

5-Bromobenzimidazolone (2g) [13]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.74 (s, 2H), 7.08 – 7.05 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.52, 131.71, 129.49, 123.37, 112.47, 111.51, 110.54.

N-Phenylbenzimidazolone (2h) [13]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.70 – 7.35 (m, 5H), 7.14–6.94 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.71, 135.09, 130.50, 129.84, 128.95, 127.75, 126.37, 122.25, 121.33, 109.63, 108.57.

5-Benzoylbenzimidazolone (2i) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.09 (s, 2H), 10.86 (s, 1H), 7.72–7.67 (m, 2H), 7.64–7.62 (m, 1H), 7.56–7.54 (m, 2H), 7.44–7.42 (m, 1H), 7.34 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 195.44, 155.87, 138.70, 134.51, 132.24, 130.16, 129.90, 129.62, 128.79, 124.89, 110.19, 108.44.

5,5-Bibenzimidazol-2,2-dione (2j) [14]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.64 (d, *J* = 9.8 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (s, 2H), 6.97 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.91, 134.33, 130.86, 129.24, 119.55, 109.22, 107.01.

2-Benzothiazolone (2k) [13]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.88 (s, 1H), 7.57-7.54 (m, 1H), 7.32–7.23 (m, 1H), 7.19 – 7.08 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.46, 136.80, 126.86, 123.77, 123.15, 123.05, 111.94.

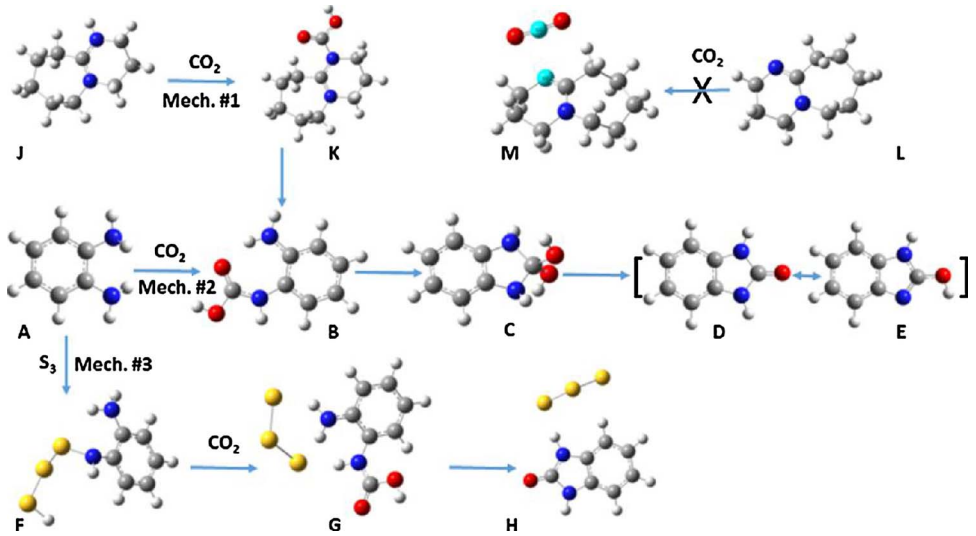

Fig. 1. Three mechanisms were proposed for the synthesis of benzimidazolone by fixing CO_2 at atmospheric pressure.