

## Remarkably Efficient Catalysts of Amidine Hydroiodides for the Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides under Mild Conditions

Naoto Aoyagi, Yoshio Furusho, and Takeshi Endo\*

Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555

(Received December 12, 2011; CL-111185; E-mail: tendo@moleng.fuk.kindai.ac.jp)

Hydroiodides of amidines effectively catalyzed the reaction of CO<sub>2</sub> and epoxides under mild conditions such as ordinary pressure and ambient temperature, and the corresponding 5-membered cyclic carbonates were obtained in moderate to high yields.

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere is partly responsible for climate change, while CO<sub>2</sub> is also regarded as a cheap, green C1 resource.<sup>1</sup> One of the most important processes is incorporation of CO<sub>2</sub> into epoxides to give five-membered cyclic carbonates, which are widely used as starting compounds for various materials.<sup>2</sup> A wide range of CO<sub>2</sub>-incorporation catalysts for the synthesis of cyclic carbonates have been developed, including alkali metal salts,<sup>3</sup> onium salts,<sup>4</sup> metal complexes,<sup>5</sup> ionic liquids,<sup>6</sup> and so on. However, most of these catalytic systems require high pressure and/or high temperature for achieving high efficiency with the exception of several expensive metal catalysts. In addition, some of them suffer from the formation of poly- and oligocarbonates as by-product. We have recently reported that the LiBr-catalyzed reaction of CO<sub>2</sub> and epoxides is highly accelerated in the presence of *N*-methyltetrahydropyrimidine (MTHP) as a CO<sub>2</sub> carrier, and the corresponding cyclic carbonates are obtained in moderate to high yields under mild conditions (1 atm, r.t. to 45 °C).<sup>7</sup> However, this system requires large amounts of LiBr as well as MTHP for obtaining the carbonates in reasonable yields. Over the course of our program to develop CO<sub>2</sub>-capturing materials based on amidines such as MTHP,<sup>8</sup> we have found that hydroiodides of amidines efficiently catalyze the cyclic carbonate-forming reactions from CO<sub>2</sub> and epoxides (Chart 1). Herein we report a novel efficient synthetic method of cyclic carbonates from CO<sub>2</sub> and epoxides by using a catalytic amount of hydroiodides of amidines<sup>9</sup> under mild conditions such as ordinary pressure and ambient temperature (Scheme 1).

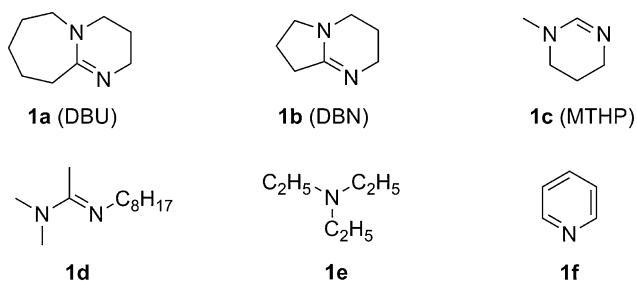
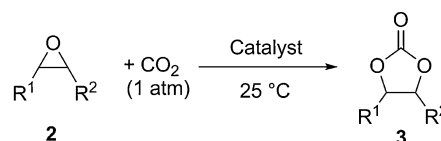


Chart 1. Amidines and amines used in this study.

First, we investigated the effect of the counter anions of the salts of **1a** (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) on the carbonate formation from phenyl glycidyl ether (**2a**) and CO<sub>2</sub> in



a: R<sup>1</sup> = PhOCH<sub>2</sub>, R<sup>2</sup> = H      d: R<sup>1</sup> = CH<sub>2</sub>=C(CH<sub>3</sub>)COOCH<sub>2</sub>, R<sup>2</sup> = H  
b: R<sup>1</sup> = *n*-C<sub>4</sub>H<sub>9</sub>OCH<sub>2</sub>, R<sup>2</sup> = H      e: R<sup>1</sup> = Ph, R<sup>2</sup> = H  
c: R<sup>1</sup> = ClCH<sub>2</sub>, R<sup>2</sup> = H

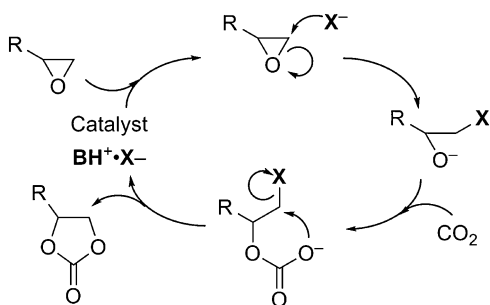
**Scheme 1.** Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.

**Table 1.** Effect of counter anions of amidinium salts on the synthesis of the cyclic carbonate **3a** from **2a** and CO<sub>2</sub> (1 atm) in the presence of amidinium halides (5 mol %) at 25 °C for 24 h

Entry	Catalyst	Yield/% <sup>c</sup>
1	<b>1a</b> ·HOAc	<1
2	<b>1a</b> ·HCl	4.0
3	<b>1a</b> ·HBr	33
4	<b>1a</b> ·HI	95
5	HI <sup>d</sup>	N.D. <sup>e</sup>

<sup>a</sup>[**2a**] = 5.0 M. <sup>b</sup>MeTHF: 2-Methyltetrahydrofuran. <sup>c</sup>Determined by <sup>1</sup>H NMR. <sup>d</sup>NMP (1-Methyl-2-pyrrolidinone) was used as solvent. <sup>e</sup>Not detected.

MeTHF (2-methyltetrahydrofuran) at 1 atm and ambient temperature (Table 1). It has recently been reported that the acetate (**1a**·HOAc) and the chloride (**1a**·HCl) catalyze the reaction of propylene oxide and CO<sub>2</sub> under relatively severe conditions such as 10 atm and 140 °C.<sup>6d</sup> However, neither **1a**·HOAc nor **1a**·HCl gave much cyclic carbonate (**3a**) at 1 atm and 25 °C for 24 h (Entries 1 and 2). In contrast, the use of the bromide (**1a**·HBr) resulted in an increased yield of 33%, and the yield was remarkably increased up to 95% when the iodide (**1a**·HI) was used as the catalyst (Entries 3 and 4). The catalysis is thus highly affected by the leaving ability of the counter anion moiety of the amidinium salt. Therefore, the leaving of iodide anion at the ring-closure step is most likely to be the rate-determining step for the reaction. A plausible mechanism for the catalytic synthesis of carbonates consists of nucleophilic attack of the halide anion to the epoxy group followed by carbonate formation with CO<sub>2</sub> and subsequent ring-closing reaction (Scheme 2). The catalytic cycle does not involve activation of the epoxide by the acidic moiety of the catalyst, which was confirmed by the <sup>1</sup>H NMR spectrum of a solution of **2a** and **1a**·HI in CD<sub>3</sub>CN that showed no chemical shift change of the



**Scheme 2.** A plausible mechanism for catalyzed synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>.

**Table 2.** Synthesis of the cyclic carbonate **3a** from the epoxide **2a** (5.0M) and CO<sub>2</sub> (1 atm) in the presence of various amidinium or ammonium iodides **1** (5 mol %) in MeTHF<sup>a</sup> at 25 °C for 24 h

Entry	Catalyst	Yield/% <sup>b</sup>
1	<b>1a</b> ·HI	95
2	<b>1b</b> ·HI	91
3	<b>1c</b> ·HI	76
4	<b>1d</b> ·HI	76
5	<b>1e</b> ·HI	29
6	<b>1f</b> ·HI	9.1

<sup>a</sup>2-Methyltetrahydrofuran. <sup>b</sup>Determined by <sup>1</sup>H NMR.

**Table 3.** Synthesis of various cyclic carbonates **3a–3d** from the epoxide **2a–2d** with CO<sub>2</sub> (1 atm) by using **1a**·HI (5 mol %) at 25 °C for 24 h

Entry	Epoxide	Carbonate	Solvent	Yield/% <sup>c</sup>
1	<b>2a</b>	<b>3a</b>	THF <sup>a,b</sup>	97
2	<b>2b</b>	<b>3b</b>		67
3	<b>2c</b>	<b>3c</b>		85
4	<b>2d</b>	<b>3d</b>		78
5	<b>2e</b>	<b>3e</b>		38
6	<b>2b</b>	<b>3b</b>	bulk	86
7	<b>2c</b>	<b>3c</b>		95
8	<b>2d</b>	<b>3d</b>		95
9	<b>2e</b>	<b>3e</b>		64

<sup>a</sup>[**2**] = 5.0 M. <sup>b</sup>Tetrahydrofuran. <sup>c</sup>Determined by <sup>1</sup>H NMR.

proton signals. In fact, no carbonate was formed in the presence of hydrogen iodide (Entry 5).

Next, we investigated the effect of the structures of the catalysts on the carbonate-forming reaction of **2a** and CO<sub>2</sub> in MeTHF as shown in Table 2. For the amidinium iodides with bicyclic structure (**1a**·HI and **1b**·HI), the yields of the carbonate **3a** surpassed 90% (Entries 1 and 2). The use of the monocyclic amidinium iodide (**1c**·HI) or the linear amidinium salt (**1d**·HI) resulted in decreased yields (Entries 3 and 4). In contrast, the ammonium salts of triethylamine or pyridine (**1e**·HI and **1f**·HI) afforded **3a** in very low yields, which indicate that the high basicity of the amidine moiety is prerequisite for the catalysis (Entries 5 and 6).

Furthermore, we examined the carbonate-forming reactions of other epoxides with **1a**·HI (Table 3). Butyl glycidyl ether

(**2b**), epichlorohydrin (**2c**), and glycidyl methacrylate (**2d**) gave the corresponding carbonates **3b–3d** in lower yields than that for the reaction of **2a** (Entries 1–4). 4-Phenyl-1,3-dioxolan-2-one (**3e**) was obtained in a low yield, which could be attributed to the low reactivity of styrene oxide (**2e**) due to steric hindrance around the epoxy group (Entry 5).<sup>12</sup> The carbonate-forming reactions proceeded without solvent and afforded the carbonates in higher yield than those in THF (Entries 6–9).

In summary, we have demonstrated that the hydroiodides of the amidines catalyze effectively the reactions from CO<sub>2</sub> and the epoxides and the corresponding 5-membered cyclic carbonates are obtained in reasonable yields under mild conditions such as ordinary pressure and ambient temperature, highlighting that the catalysis by the hydroiodides of the amidines overwhelms those by the other hydrohalide counterparts.

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