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Amidine-mediated delivery of CO_2 from gas phase to reaction system for highly efficient synthesis of cyclic carbonates from epoxides

Balaka Barkakaty, Kazuhide Morino, Atsushi Sudo and Takeshi Endo*

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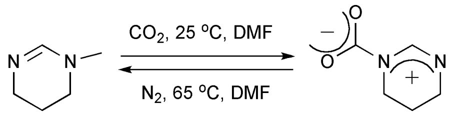
A novel, efficient synthesis of cyclic carbonates from the reaction of epoxides and gaseous CO_2 under mild conditions (1 atm, rt to 45 °C) was achieved in reasonable yields (65–83%) by using *N*-methyltetrahydropyrimidine (MTHP) that facilitated efficient delivery of CO_2 from the gas phase to the reaction system.

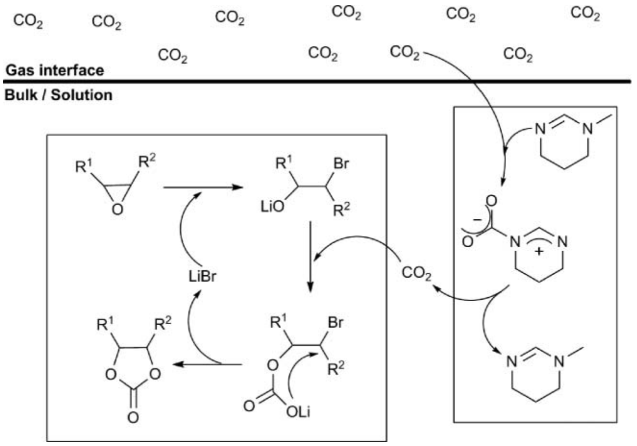
Introduction

Innovation of novel methods for easy and economical chemical fixation of CO_2 and its use as a C1 resource for synthesis of valuable target molecules is the need of this century for the sustenance of life on earth.[1] Recently, the synthesis of five-membered cyclic carbonates from epoxides using CO_2 has gained much attention, owing to its increased importance as a building block in polymer synthesis, electrolytes, aprotic polar solvents and precursors for pharmaceuticals.[2] For this reaction, various catalysts, including metal complexes,[3] smectites,[4] titanosilicates,[5] zeolites,[6] metal oxides,[7] organic bases,[8] alkali metal halides[9] and ionic liquids,[10] have already been developed and reported. However, high pressure and/or high temperature are important pre-requisites for high efficiency in these catalytic systems, and some of them suffer from the formation of poly(carbonate) as a by-product. Endo and coworkers have reported that alkali metal salts such as lithium bromide catalyzed the reaction at 1 atm pressure to give five-membered cyclic carbonates in high yields and without the formation of poly(carbonate).[9] However, in order to achieve a satisfactory rate of reaction, heating the system to 100 °C was required. In other words, catalysis of the reaction at 1 atm and at near ambient temperature is still a highly challenging endeavour. Recently, Endo and coworkers have reported a reversible system for efficient trap-and-release of $CO_2(g)$ by *N*-methyltetrahydropyrimidine (MTHP) and its analogous functionality attached to polymer side chains (Scheme 1).[11]



Scheme 1 Reversible fixation-release of CO_2 by amidine (MTHP).

This intrinsic nature of MTHP prompted us to design a new system for converting epoxides into the corresponding carbonates under milder temperature conditions and at atmospheric pressure, which relies on utilization of MTHP that can naturally capture CO_2 molecules from the gas phase and deliver them to the reactive site in a reversible cycle (Scheme 2).

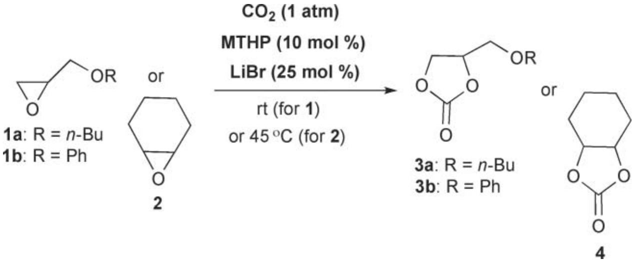


Scheme 2 Delivery of CO_2 by amidine and its insertion reaction with epoxide.

Herein, we report our achievement of a highly efficient utilization of CO_2 at low temperature (<45 °C) and under 1 atm, which was facilitated by participation of MTHP as a "CO_2 deliverer".

Results and discussion

For the present study, two monosubstituted epoxides, *n*-butyl glycidyl ether (**1a**), glycidyl phenyl ether (**1b**), and one sterically hindered disubstituted epoxide, cyclohexene oxide (**2**), were employed as substrates (Scheme 3). The reactions were carried out at 25 or 45 °C, which were much lower than the previously



Scheme 3 Amidine catalyzed synthesis of cyclic carbonates from epoxides under mild conditions.

Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka, 820-8555, Japan.
E-mail: tendo@mol-eng.fuk.kindai.ac.jp; Fax: +81-948-22-7210; Tel: +81-948-22-7210

Table 1 Synthesis of cyclic carbonates from epoxides[a]

Entry	Substrate/ product	Amount of MTHP/mol%	Time/h	*T*/°C	Yield/%[b]
1	**1a/3a**	0	6	25	48
2	**1a/3a**	10	6	25	100 (77)
3[c]	**1a/3a**	10	6	25	0
4[d]	**1b/3b**	0	96	25	45
5[d]	**1b/3b**	10	24	25	35
6[d]	**1b/3b**	10	96	25	100 (83)
7	**2/4**	0	72	45	12
8	**2/4**	10	12	45	25
9	**2/4**	10	24	45	68
10	**2/4**	10	48	45	84
11	**2/4**	10	72	45	95 (65)

[a] Conditions: [epoxide]$_0$: [MTHP] : [LiBr] = 100 : 10 : 25. [b] Determined by 1H NMR. Isolated yields are shown in parentheses. [c] Reaction carried out in the absence of LiBr. [d] Reaction carried out in NMP, the initial concentration of epoxide was 1 M.

reported temperature (100 °C)[9] for the efficient transformation of epoxide into the corresponding carbonate by using lithium bromide as catalyst under 1 atm CO_2. The results are summarized in Table 1.

The reaction of **1a** was studied first. As a reference experiment, the reaction was performed in the absence of MTHP (entry 1); when a bulk mixture of **1a** and LiBr (25 mol%) was stirred at room temperature in a reaction vessel equipped with a 1 atm CO_2 balloon, **1a** was slowly converted into the corresponding cyclic carbonate **3a**, and after 6 h, its yield, determined by ^{1}H NMR analysis of the resulting mixture, had reached 48%. On the other hand, the addition of 10 mol% MTHP under similar conditions remarkably improved the efficiency of the reaction to allow complete conversion of **1a** into **3a** after 6 h (entry 2). However, use of LiBr was mandatory for the reaction; in its absence, the reaction fails to proceed (entry 3).

This remarkable acceleration was also observed on adding MTHP in the reaction of epoxide **1b** (entry 4 *vs.* entry 5). In this case, use of a solvent was required, because the intrinsically high crystallinity of the corresponding carbonate product **3b** prevented efficient progress of the reaction in the bulk state. *N*-Methylpyrrolidone (NMP) was used as a suitable solvent which allowed the reaction to proceed in the homogeneous system.[9] In the absence of MTHP, only 45% yield of the corresponding cyclic carbonate **3b** was achieved, even though the reaction time was prolonged to 96 h (entry 4). In contrast, by adding MTHP, the reaction was greatly accelerated to achieve 100% yield of **3b** under the same reaction conditions (entry 6).

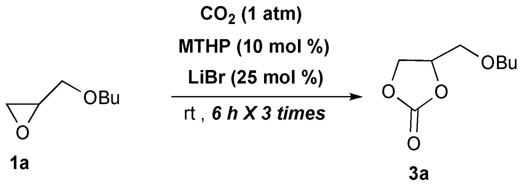
These successful results at low temperature encouraged us further to apply the MTHP-mediated system for the reaction of cyclohexene oxide **2** (Table 1, entries 8–11). So far, transformation of such 1,2-disubstituted epoxides into the corresponding carbonates by conventional systems has been rather difficult due to steric hindrance.[3d,3g,8c,10a,10e] For example, when cyclohexene oxide **2** was heated in NMP (at 100 °C, for 24 h) under 1 atm CO_2, the reaction was quite slow, leading to only 35% yield of the carbonate **4**. This poor efficiency implied the intrinsic low reactivity of **2**, and, in fact, its bulk reaction at 45 °C in the absence of MTHP was also very slow, giving the corresponding carbonate **4** in only 12% yield after 72 h (entry 7). In contrast, by adding MTHP, the efficiency of the reaction was improved markedly. The yield of **4** reached 25% after 12 h (entry 8), followed by a smooth progress of the reaction to achieve 95% yield at 72 h (entries 8–11).

Table 2 Reusability of MTHP–LiBr system

Entry	Recycle number	Yield/%[a]
1	Fresh	100
2	Recycle 1	46
3	Recycle 2	22

[a] Determined by ^{1}H NMR.

However, the catalytic efficiency of the catalysts showed a gradual decrease when recycled (Scheme 4, Table 2). This might be attributed to the gradual decrease of LiBr concentration during the process of product separation by filtration and repeated washing with diethyl ether. Since Li salts are known to have a high affinity for carbonate and ether compounds,[12] succesive formation of carbonate products followed by further treatment with diethyl ether probably removes substantial amounts of the required LiBr catalyst from the reaction system, resulting in lower yields of the desired products when the same loadings of catalysts were reused.



Scheme 4 Synthesis of butylglycidyl carbonate from recycled catalysts.

Conclusion

In summary, a highly efficient synthesis of cyclic carbonates from the corresponding epoxides was designed and achieved by utilizing only a catalytic amount of natural CO_2 fixer like MTHP along with the conventional LiBr catalyst. This system broadens the scope of such reactions by outlining a key concept to overcome the high activation barrier which is faced by these reactions when using conventional methodologies employing high temperature and high pressure techniques. The reported method can be operated successfully at atmospheric pressure and at 25–45 °C, which allows less energy-demanding and more environmentally friendly chemical fixation of CO_2 into valuable compounds. The successful results imply that addition of MTHP as a "CO_2 deliverer" might be a versatile strategy to improve the efficiency of various reaction systems which use CO_2 as a reactant.

Experimental

a) The experimental procedure for the synthesis of 3a

CO_2(g) from a gas balloon (purchased from AS ONE, code 9-086-01) was allowed to react with 10 mol% of MTHP (25 mg, 0.25 mmol) at room temperature for 25 min, after which the liquid MTHP turned into white solid. Then, 25 mol% of LiBr (55 mg, 0.64 mmol) followed by 2.55 mmol of *n*-butyl glycidyl ether (**1a**, 0.36 ml) were added to the reaction mixture and the reaction was allowed to stir at room temperature under CO_2 atmosphere (1 atm) for another 6 h. ^{1}H NMR of the crude reaction mixture in $CDCl_3$ showed 100% conversion of the starting epoxide to the desired carbonate compound after 6 h. Diethyl ether (5 ml) was then added to the reaction mixture and the reaction mixture was allowed to stir for around 10 min in the open air, the liquid part was then separated from the suspension by simple filtration. The residue in the reaction vessel was scratched with a spatula and washed several times with diethyl ether and filtered to ensure removal of any carbonate product trapped in the white solid suspension. Then, the combined filtrate was evaporated to obtain 360 mg of pure *n*-butyl glycidyl carbonate (**3a**) in 81% yield.[13]

b) The experimental procedure for the synthesis of 3b

CO_2(g) from a gas balloon (purchased from AS ONE, code 9-086-01) was allowed to react with 10 mol% of MTHP (25 mg, 0.25 mmol) in 2.5 mL of NMP at room temperature for 25 min. Then, 25 mol% of LiBr (55 mg, 0.64 mmol) followed by 2.55 mmol of phenyl glycidyl ether (**1b**, 0.35 ml) were added to the reaction mixture and the reaction was allowed to stir at room temperature under CO_2 atmosphere (1 atm) for another 96 h. ^{1}H NMR of the crude reaction mixture in $CDCl_3$ after 96 h showed 100% conversion of the starting epoxide to the desired carbonate compound. The reaction mixture was then poured into 100 mL of water and the precipitate was washed thoroughly with water. The crude cyclic carbonate was then recrystallized from ethanol to obtain 411 mg of pure phenyl glycidyl carbonate (**3b**) in 83% yield.[9a]

c) The experimental procedure for the synthesis of 4

CO_2(g) from a gas balloon (purchased from AS ONE, code 9-086-01) was allowed to react with 10 mol% of MTHP (200 mg, 2.04 mmol) at room temperature for 25 min, after which the liquid MTHP turned into white solid. Then, 25 mol% of LiBr (443 mg, 5.1 mmol) followed by 20.04 mmol of cyclohexene oxide (**2**, 2.0 ml) were added to the reaction mixture and the reaction was allowed to stir at 45 °C under CO_2 atmosphere for 72 h. After 72 h, the reaction mixture turned into a gel-like precipitate. ^{1}H NMR of the crude reaction mixture in $CDCl_3$ after 72 h showed 95% conversion of the starting epoxide to the desired carbonate compound. Then, the crude reaction mixture was extracted with EtOAc–H_2O followed by a further three extractions of the aqueous layer with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography [hexane–EtOAc (3/2, v/v)] to give 1.85 g of **4** (65% yield).[14]

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