BULLETIN OF THE
KOREAN CHEMICAL SOCIETY

TBD/Alkyl Halide-catalyzed Synthesis of Cyclic Carbonates from CO_2

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Received December 1, 2015, Accepted December 30, 2015, Published online March 14, 2016

Keywords: Carbonate, CO_2, 1,5,7-triazabicyclo[4.4.0]dec-5-ene

Developing methods for the chemical conversion of CO_2 to valuable organic compounds is considered one of the methods for reducing the level of CO_2 in the atmosphere and expanding the industrial utilization of CO_2-conversion products.[1] Cyclic carbonates, which are common CO_2-conversion products, are extensively used in polymerization[2] and Li-ion batteries;[3] therefore, tremendous effort has been devoted to preparing these products from CO_2 under environmentally benign and economical reaction conditions. Heterogeneous catalysts, such as metal oxides, zeolites, and metal complexes, along with homogeneous metal-free conditions have been used to promote the coupling of diols to CO_2 for producing industrially useful carbonates.[4,5] The metal- and ammonium/phosphonium-catalyzed addition of CO_2 to epoxides produces five-membered cyclic carbonates with various substituents.[2,6,7]

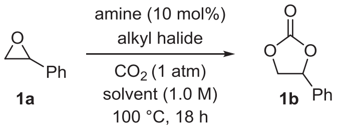
In addition to the use of metal-free conditions through ammonium/phosphonium catalysis, reactive CO_2 activators like amidines and guanidines are also used for carbonate synthesis,[8] wherein the nitrogen in these compounds reacts with CO_2 to form a zwitterionic carbamate as a key intermediate for further CO_2 conversion reactions.[9] Furthermore, the protonation of amidines and guanidines facilitates the reaction between CO_2 and epoxides, because the cationic tertiary nitrogen of the protonated amidines and guanidines forms a hydrogen bond with the oxygen of the epoxide, resulting in facile ring-opening of epoxides for carbonate formation. Protonated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) have been used for this purpose. In this study, we present the TBD-catalyzed coupling of CO_2 and epoxides in the presence of catalytic amounts of alkyl halides. Compared with previous studies, no acid is required to form protonated TBD. Furthermore, the TBD/alkyl halide-catalyzed reaction is carried out under mild reaction conditions (1 atm of CO_2) in modest to good yields.

The optimization of the synthesis of **1b** is summarized in Table 1. The reaction of styrene oxide **1a** with CO_2 (1 atm) was carried out in the presence of TBD (10 mol%) and 1-iodooctane (10 mol%) in dioxane at 100 °C to afford cyclic carbonate **1b** in 52% yield (entry 1). By increasing the amount of iodooctane to 20 and 30 mol%, the yield was increased up to 79% (entries 2 and 3). Besides dioxane, we also screened other solvents (entries 4–6). Toluene, *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamdie (DMAc) afforded **1b** in 78% yield, 51% yield, and trace amounts, respectively. Next, various guanidines, amidines, and amines were evaluated. 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (Me-TBD) catalyzed the reaction to give **1b** in 82% yield (entry 7), which is comparable with the TBD-catalyzed reaction. 1,1,3,3-Tetramethylguanidine (TMG) formed **1b** in trace amounts (entry 8). Other amidine catalysts, DBU and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were used to form **1b** in 77 and 42% yield, respectively (entries 9 and 10). *N*-Methylbenzylamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), and *N*,*N*-dimethylaminopyridine (DMAP) catalyzed the desired cyclic carbonate formation, albeit in low yields compared with TBD and DBU (entries 11–13). Instead of 1-iodooctane, 1-bromooctane was applied to give a similar yield of **1b**, while iodocyclohexane decreased the yield to 58% (entries 14 and 15). Tetra-*n*-butylammonium iodide (TBAI) is known to catalyze the reaction of CO_2 with epoxides to afford cyclic carbonates at high temperature and pressure[7a,e,h,i]; thus, TBAI was applied instead of the combination of 1-iodooctane and strong organic bases, but only a trace amount of **1b** was formed under 1 atm of CO_2 (entry 16). The combination of TBD and TBAI provided **1b** in lower yield compared with the reaction using 1-iodooctane and TBD (entries 4 and 17). In the absence of an alkyl halide, neither TBD nor Me-TBD promoted the desired cyclic carbonate formation under 1 atm of CO_2 (entry 18).

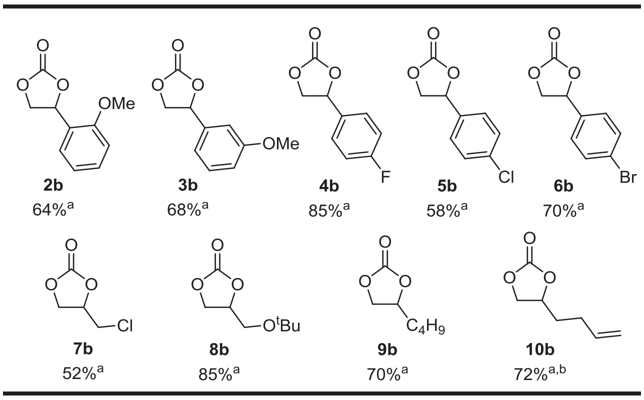
Using these optimized conditions (Table 1, entry 4), various epoxides were examined to afford the corresponding cyclic carbonates (Figure 1). 2-Methoxy- and 3-methoxy-substituted styrene oxides afforded **2b** and **3b** in 64 and 68% yield, respectively. Halogen (F, Cl, and Br)-substituted styrene oxides participated in the reaction to form the desired products in good yield (85, 58, and 70% yield). Aliphatic oxiranes were also tested. Chloro-substituted cyclic carbonate **7b** was formed in 52% yield, and *tert*-butoxy methylene- and alkyl-substituted carbonates (**8b**, **9b**, and **10b**) were formed in good yields.

A reaction mechanism for this transformation is proposed in Scheme 1. The role of 1-iodooctane is that of a halide

Table 1. Synthesis of cyclic carbonate **1b**

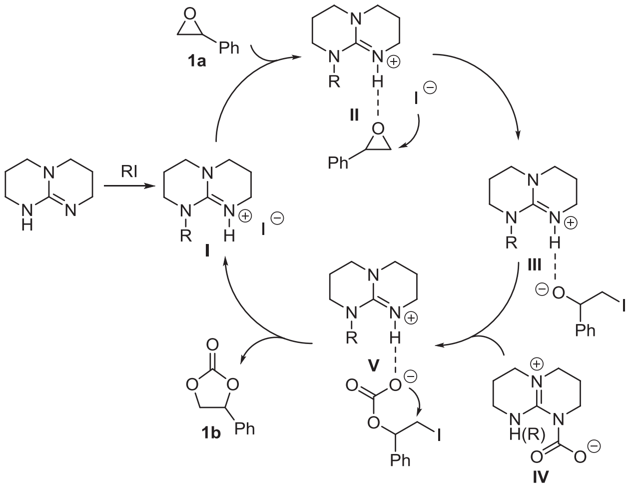


Entry	Alkyl halide	Amine	Solvent	Yield[a]
1	1-Iodooctane (10 mol%)	TBD	Dioxane	52%
2	1-Iodooctane (20 mol%)	TBD	Dioxane	70%
3	1-Iodooctane (30 mol%)	TBD	Dioxane	79%
4	1-Iodooctane (30 mol%)	TBD	Toluene	78%
5	1-Iodooctane (30 mol%)	TBD	DMF	51%
6	1-Iodooctane (30 mol%)	TBD	DMAc	Trace
7	1-Iodooctane (30 mol%)	Me-TBD	Dioxane	82%
8	1-Iodooctane (30 mol%)	TMG	Dioxane	Trace
9	1-Iodooctane (30 mol%)	DBU	Dioxane	77%
10	1-Iodooctane (30 mol%)	DBN	Dioxane	42%
11	1-Iodooctane (30 mol%)	*N*-methylbenzylamine	Dioxane	3%
12	1-Iodooctane (30 mol%)	DABCO	Dioxane	39%
13	1-Iodooctane (30 mol%)	DMAP	Dioxane	43%
14	1-Bromooctane (30 mol%)	TBD	Dioxane	77%
15	Iodocyclohexane (30 mol%)	TBD	Dioxane	58%
16	TBAI (30 mol%)	—	Dioxane	Trace
17	TBAI (30 mol%)	TBD	Dioxane	53%
18	—	TBD (Me-TBD)	Dioxane	N.R.



[a]isolated yield, [b]1-Iodooctane (10 mol%) was used.

Figure 1. Synthesis of various carbonates from CO_2.



Scheme 1. Plausible catalytic cycle.

source for the ring-opening of the epoxide. A cationic ammonium iodide I is generated by the reaction of TBD and iodooctane (RI),[10] wherein the protonated amine forms a hydrogen bond with epoxide **1a** and the proximal iodide anion is added to **1a**. Intermediate III reacts with the zwitterionic TBD–CO_2 IV complex to provide V, which undergoes intramolecular substitution to afford the desired product **1b** and regenerate I.

In summary, a combination of TBD and alkyl halide (iodooctane) was found to produce cyclic carbonates from CO_2 and epoxides. The role of halide ions in the cyclic carbonate synthesis is already known, but previously reported ammonium halide-catalyzed carbonate syntheses required harsh reaction conditions; most reactions are carried out above 10 atm of CO_2. In this study, without using strong acid, the catalytically competent ammonium halides were generated *in situ* by mixing TBD and an alkyl halide. The activated TBD–alkyl halide complex was used to synthesize various cyclic carbonates in modest to good yields.

Experimental

Representative procedure for the synthesis of carbonates: styrene oxide (57 μl, 0.5 mmol) and TBD (7 mg, 0.05 mmol) was added to a solution of 1-iodooctane (27 μl, 0.15 mmol) in 1,4-dioxane (1.0 M, 0.5 ml). A slow stream of CO_2 was passed through this solution for 1 min. Then, the reaction mixture was stirred at 100 °C for 18 h under CO_2 atmosphere. The solvent was evaporated, and the residue was purified by flash silica gel column chromatography (20% ether/hexane) to afford 4-phenyl-1,3-dioxolan-2-one **1b** (64.5 mg, 79 %). Compounds **1b-10b** were previously reported.[6,11]

Acknowledgments. This study was supported by the Korea Research Foundation (no. 2013008819) and the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant by the Korea Government Ministry of Trade, Industry & Energy (no. 20154010200820).

References

1. For recent review articles on conversion of carbon dioxide to organic compounds, see: (a) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; (b) M. Aresta, A. Dibenedetto, *Dalton Trans.* **2007**, 2975; (c) L.-N. He, J.-Q. Wang, J.-L. Wang, *Pure Appl. Chem.* **2009**, *81*, 2069; (d) M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43; (e) S. N. Riduan, Y. Zhang, *Dalton Trans.* **2010**, *39*, 3347; (f) D. J. Darensbourg, *Inorg. Chem.* **2010**, *49*, 10765; (g) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510; (h) R. Martin, A. W. Kleij, *ChemSusChem* **2011**, *4*, 1259; (i) I. Omae, *Coord. Chem. Rev.* **2012**, *256*, 1384; (j) C. J. Whiteoak, A. Nova, F. Maseras, A. W. Kleij, *ChemSusChem* **2012**, *5*, 2032.
2. For recent review articles on the synthesis and applications or organic carbonates, see: (a) J. H. Clememts, *Ind. Eng. Chem. Res.* **2003**, *42*, 663; (b) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388; (c) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312; (d) W.-L. Dai, S.-L. Luo, S.-F. Yin, C.-T. Au, *Appl. Catal. A: Gen.* **2009**, *366*, 2; (e) B. Schäffner, *Chem. Rev.* **2010**, *110*, 4554; (f) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2015**, *8*, 2436.
3. For selected review articles on the use of carbonates as a Li-ion battery electrolyte, see: (a) D. C. Webster, *Prog. Org. Coat.* **2003**, *47*, 77; (b) D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J. S. Gnanaraj, H.-J. Kim, *Electrochim. Acta* **2004**, *50*, 247; (c) K. Xu, *Chem. Rev.* **2004**, *104*, 4303; (d) S. S. Zhang, *J. Power Sources* **2006**, *162*, 1379; (e) K. Xu, *Chem. Rev.* **2014**, *114*, 11503.
4. For heterogeneous catalyzed cyclic carbonate synthesis from diols, see: (a) J. Kizlink, I. Pastucha, *Collect. Czech. Chem. Commun.* **1995**, *60*, 687; (b) T. Sakakura, Y. Saito, M. Okano, J.-C. Choi, T. Sako, *J. Org. Chem.* **1998**, *63*, 7095; (c) J.-C. Choi, L.-N. He, H. Yasuda, T. Sakakura, *Green Chem.* **2002**, *4*, 230; (d) J.-C. Choi, K. Kohno, Y. Ohshima, H. Yasuda, T. Sakakura, *Catal. Commun.* **2008**, *9*, 1630; (e) D. C. Stoian, E. Taboada, J. Llorca, E. Molins, F. Median, A. M. Segarra, *Chem. Commun.* **2013**, *49*, 5489.
5. For metal-free carbonate synthesis from alcohols, see: (a) J.-i. Kadokawa, H. Habu, S. Fukamachi, M. Karasu, H. Tagaya, K. Chiba, *J. Chem. Soc., Perkin Trans.* **1999**, *1*, 2205; (b) M. O. Bratt, P. C. Taylor, *J. Org. Chem.* **2003**, *68*, 5439; (c) Y. Yamazaki, K. Kakuma, Y. Du, S. Saito, *Tetrahedron* **2010**, *66*, 9675; (d) Y. N. Lim, C. Lee, H.-Y. Jang, *Eur. J. Org. Chem.* **2014**, 1823.
6. For recent articles on metal-catalyzed cycloaddtion of CO_2 to epoxides, see: (a) M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J. Mol. Catal. A: Chem.* **2003**, *204/205*, 245; (b) J. Sun, S.-i. Fujita, F. Zhao, M. Arai, *Green Chem.* **2004**, *6*, 613; (c) F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng, *J. Am. Chem. Soc.* **2005**, *127*, 4182; (d) H. Yasuda, L.-N. He, T. Sakakura, C. Hu, *J. Catal.* **2005**, *233*, 119; (e) H. Yasuda, L.-N. He, T. Takahashi, T. Sakakura, *Appl. Catal. A: Gen.* **2006**, *298*, 177; (f) X. Liu, C. Cao, Y. Li, P. Guan, L. Yang, Y. Shi, *Synlett* **2012**, *23*, 1343; (g) U. R. Seo, Y. K. Chung, *Adv. Synth. Catal.* **2014**, *356*, 1955.
7. For recent articles on metal-free cycloaddtion of CO_2 to epoxides, see: (a) V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* **2002**, *4*, 2561; (b) L.-N. He, H. Yasuda, T. Sakakura, *Green Chem.* **2003**, *5*, 92; (c) J. W. Huang, M. Shi, *J. Org. Chem.* **2003**, *68*, 6705; (d) H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* **2003**, 896; (e) Y. Du, J.-Q. Wang, J.-Y. Chen, F. Cai, J.-S. Tian, D.-L. Kong, L.-N. He, *Tetrahedron Lett.* **2006**, *47*, 1271; (f) A. Sibaouih, T. Repo, *Appl. Catal., A* **2009**, *365*, 194; (g) Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai, *Org. Lett.* **2010**, *12*, 5728; (h) S. Kumar, S. L. Jain, B. Sain, *Tetrahedron Lett.* **2011**, *52*, 6957; (i) J.-Q. Wang, K. Dong, W.-G. Cheng, J. Sun, S.-J. Zhang, *Catal. Sci. Technol.* **2012**, *2*, 1480; (j) Y.-Y. Zhang, L. Chen, S.-F. Yin, S.-L. Luo, C.-T. Au, *Catal. Lett.* **2012**, *142*, 1376; (k) A. J. R. Amaral, J. F. J. Coelho, A. C. Serra, *Tetrahedron Lett.* **2013**, *54*, 5518; (l) H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu, X.-B. Lu, *J. Org. Chem.* **2008**, *73*, 8039; (m) M. J. Ajitha, C. H. Suresh, *Tetrahedron Lett.* **2011**, *52*, 5403.
8. For recent articles on guanidine/amidine-catalyzed cycloaddtion of CO_2 to epoxides, see: (a) A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* **2003**, *44*, 2931; (b) Z.-Z. Yang, L.-N. He, C.-X. Miao, S. Chanfreau, *Adv. Synth. Catal.* **2010**, *352*, 2233; (c) T. Yu, R. G. Weiss, *Green Chem.* **2012**, *14*, 209; (d) S. Foltran, J. Alsarraf, F. Robert, Y. Landais, E. Cloutet, H. Cramail, T. Tassaing, *Catal. Sci. Technol.* **2013**, *3*, 1046; (e) F. Adam, M. S. Batagarawa, *Appl. Catal. A: Gen.* **2013**, *454*, 164; (f) J. Sun, W. Cheng, Z. Yang, J. Wang, T. Xu, J. Xin, S. Zhang, *Green Chem.* **2014**, *16*, 3071; (g) S. Foltran, R. Merearu, T. Tassaing, *Catal. Sci. Technol.* **2014**, *4*, 1585.
9. (a) E. R. Pérez, D. W. Franco, *Tetrahedron Lett.* **2002**, *43*, 4091; (b) A. Wykes, S. L. MacNeil, *Synlett* **2007**, 107; (c) L. Phan, J. R. Andreatta, L. K. Horvey,

C. F. Edie, A. L. Luco, A. Mirchandani, D. J. Darensbourg, P. G. Jessop, *J. Org. Chem.* **2008**, *73*, 127; (d) F. S. Pereira, E. R. de Azevedo, *Tetrahedron* **2008**, *64*, 10097; (e) M. North, R. Pasquale, *Angew. Chem. Int. Ed.* **2009**, *48*, 2946.

10. J. R. Bell, H. Luo, S. Dai, *Tetrahedron Lett.* **2011**, *52*, 3723.

11. (a) R. D. Aher, B. S. Kumar, A. Sudalai, *Synlett* **2014**, *25*, 97; (b) C. William, W. Ross, N. M. Harrington, P. Riccardo, *Chem. Eur. J.* **2010**, *16*, 6828; (c) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan, E. Martin, A. W. Kleij, *J. Am. Chem. Soc* **2013**, *135*, 1228; (d) X. Yang, J. Wu, X. Mao, T. F. Jamison, T. A. Hatton, *Chem. Commun.* **2014**, *50*, 3245.