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Significant rate acceleration in carbonate synthesis from carbon dioxide and oxiranes using dimethyl carbonate as a recyclable medium

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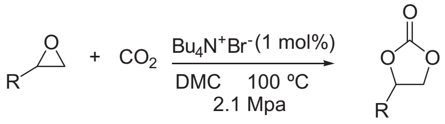
ABSTRACT

The synthesis of cyclic carbonates by the reaction of oxiranes and carbon dioxide in the presence of catalytic amount of tetrabutylammonium bromide in dimethylcarbonate without any metal catalyst is reported. Significant rate acceleration in the reaction is observed in dimethylcarbonate as compared to the other solvents. Under the reaction conditions of 100 °C and 2.1 MPa in dimethyl carbonate, maximum conversion and selectivity is achieved. The dimethylcarbonate containing tetrabutylammonium bromide catalyst can be easily recovered and reused for at least six recycles with the same selectivity.

Utilization of carbon dioxide as a renewable and environmentally friendly source of carbon for chemical transformation is of paramount importance both from C1 chemistry as well as green chemistry viewpoints.[1] Chemical fixation of carbon dioxide in the form of organic carbonates by the reaction with oxiranes is of great interest due to the wide spread applications of these compounds as synthetic intermediates, aprotic polar solvents, and as intermediates in the production of pharmaceuticals and fine chemicals.[2,3] Nevertheless, the formation of cyclic carbonates form oxiranes and carbon dioxide is an old reaction[4] and a number of inorganic and organic compounds including amines, phosphanes,[5] organotin halides,[6] transition metal complexes[7] mainly salen complexes,[8] organocatalysts,[9] ionic liquid[10] and polymer grafted ionic liquid[11] are known to catalyze this transformation. The recent challenges in chemical industry have focused on limiting the use of organic solvents or replacing them with new, environmentally benign media in a view to develop green chemical synthesis.[12] In particular, the use of dimethyl carbonate (DMC) as a non-toxic, non-corrosive, and environmentally friendly solvent is gaining particular interest in recent years.[13] However, to the best of our knowledge, there is no literature report on using DMC as reaction media for the synthesis of carbonates from the reaction of CO_2 and epoxides.

Continuing our search for new reaction media to perform organic reactions, we herein report the first successful use of dimethyl carbonate (DMC) as a recyclable reaction media as well as promoter for the synthesis of cyclic carbonates from the reaction of CO_2 with epoxides in presence of catalytic amount of tetrabutylammoium bromide (TBAB) in the absence of any metal based catalyst (Scheme 1).

At first we carried out the reaction of styrene epoxide with CO_2 in presence of TBAB (1 mol %) under solvent-free conditions at 100 °C and 2.1 MPa pressure. The reaction was found to be very slow and provided very poor yield of the corresponding carbonate even after 10 h (Table 1, entry 1). Next, we performed the reaction in a number of organic solvents including acetonitrile, CH_2Cl_2, DMC and toluene under similar reaction conditions. Surprisingly, the reaction was found to be very fast in DMC and afforded almost quantitative conversion of the desired carbonate selectively without any evidence for the formation of any by-product. Whereas the reaction was found to be very slow in dichloromethane and there was no reaction occurred in toluene (Table 1, entry 1). This observation established the promoting effect of the DMC on the reaction rate. After completion of the reaction, the reaction mixture was concentrated under vacuum to recover dimethyl carbonate. The resulting residue was diluted with diethyl ether to recover the TBAB by decantation. The combined ether layer was subjected to usual work-up to obtain the product, while the recovered DMC and TBAB catalyst were reused as such for subsequent experiments.



Scheme 1. Synthesis of carbonate under various conditions.

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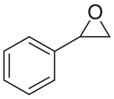
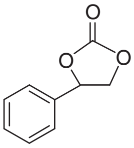
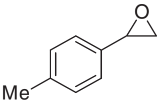
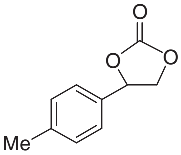
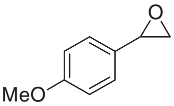
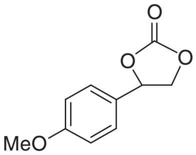
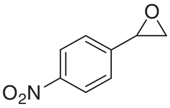
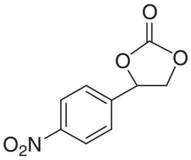
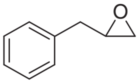
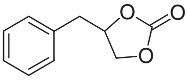
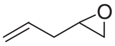
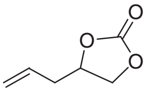
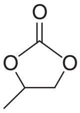
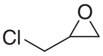
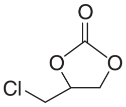
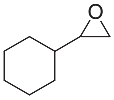
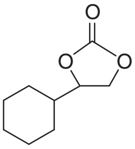
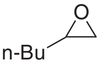
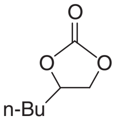
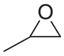
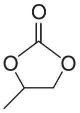
Table 1
Metal free DMC promoted coupling of epoxides with CO_2[a]

Entry	Epoxide	Product	Reaction Time (h)	Yield[b] (%)
1			6.5 12	96 45[c], 20[d], —[e] 20[f]
2			4.5	98
3			5.0	97
4			8	75
5			4.0	92
6			3.5	90
7			2.5	98
8			3.0	94
9			6.0	85
10			2.0	98
11			2.0	95

[a] Reaction conditions: substrate (10 mmol), TBAB (1 mol %, 0.1 mmol), at 100 °C under pressure 2.1 MPa in DMC (10 ml).

[b] Isolated yields.

[c] In the absence of DMC.

[d] By using dichloromethane is solvent.

[e] Using toluene as solvent.

[f] In the absence of TBAB catalyst.

The recycling of the developed catalytic system (TBAB in DCM) was checked for six runs (Fig. 1). In all the cases the conversion of the epoxide to cyclic carbonate was consistently reproducible. Thus, the use of DMC in the present reaction not only enhances the reaction rates but also provides the recycling of the catalyst.

Furthermore, the scope of the reaction was extended to various epoxides using TBAB as catalyst and DMC as reaction media under described reaction conditions.[14] The results of these experiments are summarized in Table 1. After completion of the reaction, the reaction product was isolated by extraction with diethyl ether, however TBAB immobilized in DMC can be easily recovered and reused for subsequent experiment. In a controlled experiment in DMC without using tetrabutylammonium bromide (1 mol %), the reaction was found to be very slow and a very poor yield (20%) of the desired product was obtained after 12 h. These results indicated that the presence of TBAB is essential for activation of CO_2 in the present transformation. In contrast the presence of DMC significantly increased the reaction rate and afforded almost quantitative conversion in shorter reaction time. Epoxides bearing an electron-donating substituent (Table 1, entries 2 and 3) were converted to the corresponding cyclic carbonates in high yields (95–99%) within a short reaction time (4–6 h). Whereas, epoxide with an electron-withdrawing group (Table 1, entry 4) required a longer reaction time (8 h) to give the product in a moderate yield (75%), which is probably due to the reduced electron density of the epoxide oxygen atom. In all cases, cyclic carbonates were formed exclusively; cyclic carbonate and unreacted epoxide could be obtained after the reaction. Using this protocol, the reactions could be carried out efficiently under a 2.1 MPa CO_2 pressure, making this method not perfect from synthetic viewpoints. Nevertheless, avoidance of expensive metallic catalyst, toxic and volatile organic solvent, use of environmentally benign recyclable reaction media, easy work-up and high product yields reflects the merits of the developed protocol over most of the existing ones.

The exact mechanism of the reaction is not known at this stage; however based on the known mechanism,[7c] the possible mechanism of the reaction involves the epoxide ring opening by the nucleophilic attack of bromide ion of quaternary salt. The promoting effect of dimethyl carbonate is due to its non-bonding interaction with the oxygen of epoxide,[15] which may facilitate the ring opening of the oxirane ring. The ring opening, leads to the formation of oxy anion species **2** which on subsequent reaction with carbon dioxide and subsequent cyclization may give the corresponding carbonate (Scheme 2).

In conclusion, we have demonstrated the first successful use of DMC not only as a recyclable reaction media but also its promoting effect on the reaction rates. The present reaction was carried out at 100 °C and 2.1 MPa by using TBAB (1 mol %) as catalyst under

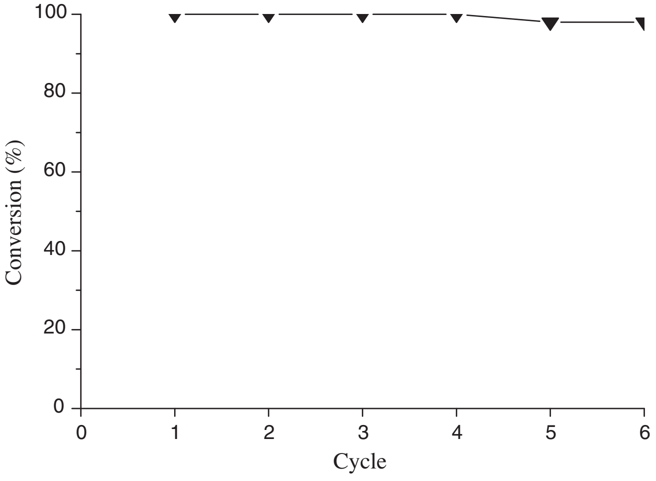
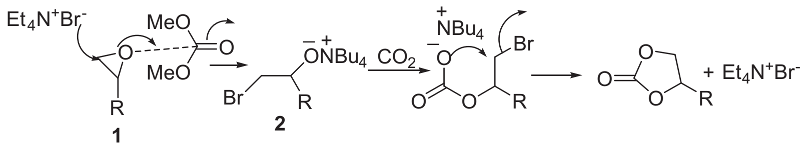


Figure 1. Results of recycling experiments.



Scheme 2. Plausible mechanism for DMC promoted synthesis of carbonates.

metal-free conditions. The DMC immobilized TBAB was successfully recycled for several runs and almost quantitative conversion were obtained with exclusive formation of cyclic carbonates without formation of any by-product. This report describes the first example of efficient use of DMC as an eco-friendly and recyclable solvent for the cyclic carbonate synthesis using carbon dioxide and oxiranes. Further applications of DMC for the chemical fixation of carbon dioxide are currently under investigation in our laboratory.

Acknowledgments

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References and notes

1. (a) Aresta, M., Ed.Carbon Dioxide as Chemical Feedstock; Wiley VCH: Weinheim, 2010; (b) Minakata, S.; Sasaki, I.; Ide, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 1309; (c) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063; (d) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27; For an exhaustive review on the subject see: (e) Aresta, M. *Carbon Dioxide Recovery Utilization*; Kluwer Academic Publisher, 2003; (f)*Carbon Dioxide Fixation and Reduction in Biological and Model Systems*; Brauden, C.-I., Schneider, G., Eds.; Oxford University Press: Oxford, UK, 1994; (g) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365.
2. (a) Schffner, B.; Schffner, F.; Verevkin, S. P.; Brner, A. *Chem. Rev.* **2010**, *110*, 4554; (b) North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12*, 1514; (c) Darensbourg, J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155; (d) Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H.; Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. *Green Chem.* **2003**, *5*, 497.
3. (a) Mizobuchi, S.; Mochizuki, J.; Soga, H.; Tanba, H.; Inoue, H. *J. Antibiot.* **1986**, *39*, 1776; (b) Chatterjee, S.; Reddy, G. C. S.; Franco, C. M. M.; Rupp, R. H.; Ganguli, B. N.; Fehlhaber, H. W.; Hans, W.; Kogler, H. *J. Antibiot.* **1987**, *40*, 1368.
4. (a) Lichtenwalter, M.; Cooper, J. U.S. Patent 2,873,282, 1959.; (b) Peppel, W. J. *Ind. Eng. Chem.* **1958**, *50*, 767.
5. Brindöpke, G.; German Pat. DE 3529263, 1987.
6. Baba, A.; Nozaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552.
7. (a) Yan, P.; Tan, X.; Jing, H.; Duan, S.; Wang, X.; Liu, Z. *J. Org. Chem.* **2011**. dx.doi.org/10.1021/jo1020294.; (b) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951; (c) North, M.; Pasquale, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2946; (d) Yan, P.; Jing, H. W. *Adv. Synth. Catal.* **2009**, *351*, 1325; (e) Jin, L.; Huang, Y.; Jing, H.; Chang, T.; Yan, P. *Tetrahedron: Asymmetry* **2008**, *19*, 1947; (f) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198–6202; (g) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725–727.
8. Paddock, R. L.; Nguyen, S. T. *Chem. Commun.* **2004**, 1622; (b) Chang, T.; Jin, L.; Jing, H. *ChemCatChem* **2009**, *1*, 379; (c) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026. and references cited therein.
9. Tsutsumi, Y.; Yamakawa, K.; Yoshida, M.; Ema, T.; Sakai, T. *Org. Lett.* **2010**, *12*, 5728.
10. Shamsuzzaman, A. A. A.; Khan, B. *Synth. Commun* **2010**, *40*, 2278.
11. Dai; Weili; Lang, C.; Shuangfeng, Y.; Wenhua, L.; Yuanyuan, Z.; Shenglian, L.; Chak-tong, A. *Catal. Lett.* **2010**, *137*, 74.
12. (a) Clark, J. H.; Tavener, S. J. *Org. Process Res. Dev.* **2007**, *11*, 149; (b) Sheldon, R. A. *Green Chem.* **2005**, *7*, 267. and references cited therein.
13. (a) Arico, F.; Tundo, P. *Usp. Khim.* **2010**, *79*, 479; (b) Bernini, R.; Mincione, E.; Barontini, M.; Crisante, F.; Fabrizic, G.; Gambacorta, A. *Tetrahedron* **2007**, *63*, 6895; (c) Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *ChemSusChem* **2008**, *1*, 813.
14. *General experimental procedure*: A 50 mL stainless steel autoclave was charged with epoxide (10.0 mmol), TBAB catalyst (0.1 mmol), DMC (10 ml) and then CO$_2$ (initial pressure of 2.1 MPa). The mixture was heated with stirring at 100 °C for the reaction time as mentioned in the Table 1. The reactor was cooled in an ice bath for 30 min, and the product was dissolved in Et$_2$O, and separated by extraction. The remained DMC layer containing TBAB was dried under vacuum and reused as such for subsequent experiment. The product was analyzed by ^{1}H NMR and GC analysis. In some cases the product was purified by silica gel column chromatography, where the conversion is not completed.
15. Selva, M. *Pure Appl. Chem.* **2007**, *79*, 1855.