## PAPER

View Article Online

Cite this: DOI: 10.1039/c3nj00640a

Received (in Porto Alegre, Brazil) 14th June 2013, Accepted 5th July 2013

DOI: 10.1039/c3nj00640a

www.rsc.org/njc

## Non-symmetrical dialkyl carbonate synthesis promoted by 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride<sup>†</sup>

Subodh Kumar and Suman L. Jain\*

An efficient synthesis of non-symmetrical dialkyl carbonates promoted by 1-(3-trimethoxysilylpropyl)-3methylimidazolium chloride ionic liquid as a reaction medium is described. The ionic liquid can easily be recovered and reused several times without significant change in the activity and selectivity.

Dialkyl organic carbonates represent an attractive and synthetically important class of organic compounds, which have been used as intermediates for the synthesis of pharmaceuticals,<sup>1</sup> fine chemicals and agrochemicals.<sup>2</sup> They also have uses as excellent polar aprotic solvents,<sup>3</sup> monomers for organic glass,<sup>4</sup> synthetic lubricants, as octane boosters for gasolines and plasticizers.<sup>5</sup> Conventional synthesis of organic carbonates involves the use of toxic and harmful chemicals, such as phosgene, pyridine and carbon monoxide.6 However, these chemicals have negative impacts on environment and health; therefore it is desired to develop alternative methodology for producing these compounds. In the recent years, symmetrical organic carbonates, especially dialkyl carbonates, have been synthesized either by carbon dioxide, epoxides and alcohols<sup>7</sup> or directly from CO<sub>2</sub> and alcohols.8 Compared to symmetrical organic carbonates, the non-symmetrical organic carbonates are more useful but more difficult to synthesize. Several methods exist that describe the synthesis of non-symmetrical carbonates, for example, ionic liquid-mediated electrochemical synthesis of organic carbonates from CO<sub>2</sub> and alcohols,<sup>9</sup> coupling of alcohols, CO<sub>2</sub> and alkyl halides in the presence of Cs<sub>2</sub>CO<sub>3</sub><sup>10</sup> and reaction of primary or secondary alcohols and CO<sub>2</sub> via unstable methanesulfonyl carbonates.<sup>11</sup> Recently, Chi and co-workers<sup>12</sup> reported the synthesis of organic carbonates via alkylation of metal carbonate with various alkyl halides and sulfonates in ionic liquids. Song et al.13 reported an organotin-oxomolybdate coordination polymer as catalyst for the synthesis of non-symmetrical organic carbonates via the transesterification of alcohols with diethyl carbonate. Dimethyl carbonate (DMC) is an environmentally benign organic compound which has widely been used in organic

synthesis as a substitute for dangerous reagents, such as phosgene and halo compounds.<sup>14</sup> In recent years, the synthesis of nonsymmetrical organic carbonates by transesterification of various alcohols with dialkyl carbonate<sup>15</sup> has attracted much attention. Several catalytic systems, including MCM-41-TBD,<sup>16</sup> Mg/La metal oxide,<sup>17</sup> CsF/Al<sub>2</sub>O<sub>3</sub>,<sup>18</sup> nanocrystalline MgO,<sup>19</sup> and metal–organic frameworks,<sup>20</sup> have been successfully developed. However, the development of highly efficient and reusable catalysts for the synthesis of non-symmetrical organic carbonates is still a very interesting topic.

Recently, synergistic catalysis involving the rate acceleration due to the presence of both acidic and basic sites has received much attention.<sup>21</sup> However, to the best of our knowledge limited reports on the synergistic effect of the functional groups in ionic liquids are disclosed in the literature. Utilization of ionic liquids is one of the goals of green chemistry as they create cleaner and more sustainable chemistry and have received increasing applications as environmental friendly solvents for many synthetic and catalytic processes. In this context Naik et al.22 reported the use of imidazolium-2-carboxylate as an efficient catalyst for the synthesis of glycerol carbonate. Recently, Selva et al.23 reported carbonate, acetate and phenolate phosphonium salts as catalysts for the synthesis of unsymmetrical carbonates by transesterification of alcohols with DMC. 1-Trimethoxysilyl propyl-3-methyl-imidazolium chloride is a famous ionic liquid, which has been extensively used for the preparation, stabilization and functionalization of catalytic support materials in order to make it recyclable for various applications.<sup>24</sup> With the aim of further exploring its potential as a recyclable reaction medium, we decided to use this ionic liquid as a promoter and reaction medium for the transesterification alcohols with dimethyl carbonate (DMC) to give the corresponding methyl carbonates.

The desired ionic liquid **1** was easily synthesized by the efficient reaction of the *N*-methylimidazole with (3-chloropropyl) trimethoxysilane at 110 °C in 97% yield (Scheme 1).<sup>24a</sup>

Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India. E-mail: suman@iip.res.in; Fax: +91-135-2660202; Tel: +91-135-2525788 † Electronic supplementary information (ESI) available. See DOI: 10.1039/

c3nj00640a



Scheme 1 The synthesis of ionic liquid 1.

$$\begin{array}{c} 0 \\ R'OH + H_3CO \\ \end{array} \begin{array}{c} 0 \\ OCH_3 \\ \end{array} \begin{array}{c} 1 \\ 80 \\ \circ C \\ \end{array} \begin{array}{c} 0 \\ R'O \\ \end{array} \begin{array}{c} 0 \\ R'O \\ \end{array} \begin{array}{c} 0 \\ OCH_3 \\ \end{array}$$

R=alkyl, alicyclic, benzyl

Scheme 2 The synthesis of non-symmetrical carbonates.

The identity of the prepared ionic liquid was established by comparing its FTIR (Fig. S1, ESI<sup>†</sup>), <sup>1</sup>H NMR (Fig. S2, ESI<sup>†</sup>) and <sup>13</sup>C NMR (Fig. S3, ESI<sup>†</sup>) spectra with the reported literature.<sup>24a</sup> The synthesized ionic liquid was found to be thermally stable up to 300 °C as ascertained by TGA analysis. The synthesized ionic liquid **1** was tested for the synthesis of unsymmetrical dialkyl carbonates *via* transesterification of various alcohols with DMC in high to excellent yields (Scheme 2).

An initial screening of different ionic liquids as mentioned in Scheme 1, was carried out on the reaction of dimethyl carbonate (DMC) and 1-butanol. The results of these experiments are reported in Table 1. The reaction was carried out by using a mixture of 1-butanol and DMC in a molar ratio of 1:1 in the presence of ionic liquid (1 ml) at 80 °C for 4 h under stirring. All the reactions were followed by GC/MS to determine the conversion

Table 1	Reaction of 1-butanol and DMC in the presence of ionic liquids <sup>a</sup>				
Entry	Ionic liquid	$\operatorname{Yield}^{b}(\%)$			
1	1	99			
2	2	61			
3	3	70			
4	4	72			
5	5	55			
6	6	50			
7	None	—			
8	<i>N</i> -Methylimidazole (NMI)	—			
9	3-Chloropropyl trimethoxysilane (CPTMS)	_			
10	<i>n</i> -Butyl chloride	—			
11	CPTMS + NMI(1:1)	30			
12	1 (2 mol%)	42			
13	1 (5 mol%)	82			
14	1 (10 mol%)	95			
15	1	$20^c$ , $65^d$			

<sup>*a*</sup> Reaction conditions: DMC (5 mmol), 1-butanol (5 mmol) at 80  $^{\circ}$ C, reaction time 4 h. <sup>*b*</sup> Yields were determined by GC. <sup>*c*</sup> Reaction was carried out at room temperature. <sup>*d*</sup> At 50  $^{\circ}$ C.

of the 1-butanol to butyl methyl carbonate. Among the two IL's i.e. 1 and corresponding 1-butyl-3-methyl imidazolium chloride 2 Table 1 (entries 1-2), siloxyl-containing ionic liquid 1 exhibited higher efficiency and afforded higher yield of the desired product. This finding illustrated the synergistic effect of the trimethoxysilyl moiety in the ionic liquid to enhance the reaction, probably by the formation of a reaction centre within the ionic liquid via interaction of the silicon atom with reactants. The reaction of 1-butanol with DMC was also performed in other ionic liquids (3-6), as shown in Scheme 1. Among all the ionic liquids studied, ionic liquid 1 was found to be better than all the others. To the best of our knowledge, this is the first application of siloxy-containing imidazolium based ionic liquid to assist the transesterification of alcohols with dialkyl organic carbonates. No reaction was observed in the absence of IL 1 and the original substrates were recovered even after a prolonged reaction time (Table 1, entry 7). Similarly, the reaction did not occur when the precursors of the synthesized ionic liquid, such as N-methyl imidazole, trimethoxysilane and n-butyl chloride, were used as the catalysts (Table 1, entries 8-10). However, when trimethoxysilane and N-methyl imidazole in equimolar (1:1) amounts were used at the same time, the reaction was found to occur but afforded only 30% yield of the desired product (Table 1, entry 11). During the present investigation, the reactions took place in the presence of ionic liquid (1 ml) as the reaction medium. However, to evaluate the catalytic effect of IL 1, the reaction between 1-butanol and DMC was studied in the presence of different amounts of 1 (Table 1, entries 12-14). The yield of butyl methyl carbonate increased with increasing the amount of the ionic liquid. The product was obtained in 95% yield when 10 mol% of IL 1 was utilized. These studies suggested a catalytic effect of IL 1 for this reaction. Next we studied the effect of reaction temperature. The reaction was found to be very slow at room temperature. However, the yield of the desired product increased with increasing the temperature and 80  $^\circ\mathrm{C}$  was found to be optimum for the reaction (Table 1, entry 15). Further increase in temperature from 80 to 100 °C did not improve the reaction to any significant extent.

On the basis of this finding we could conclude that ionic liquid **1** was the best promoter and therefore was used further for the reactions of DMC with different alcohols, including alkyl, cyclic, and aryl alcohols. The results of these experiments are summarized in Table 2. The reactivity of the primary alkyl alcohols was found to be very high and they were all transformed

Table 2 Synthesis of non-symmetrical organic carbonates from DMC and various alcohols by using ionic liquid  $1^a$ 

Entry	Substrate	Product	Time	Yield <sup>b</sup> (%)
1	ОН	о осна	4.0	98
2	∕ (H <sub>2</sub> OH	∼t→2 0 CH3	4.0	98
3	∕СУ_ОН		4.0	98
4	<pre> //<sub>5</sub> OH </pre>	√ Y <sub>5</sub> O OCH <sub>3</sub>	4.0	97
5	OH		4.5	96
6	ОН	O CCH3	6.0	97
7	CH <sub>2</sub> OH	CH20 CH3	5.0	99
8	CH <sub>2</sub> OH CH <sub>3</sub>	CH2O CH3	5.0	99
9	CH <sub>2</sub> OH	CH40 CH3	5.0	99
10	CH <sub>2</sub> OH	CH <sub>2</sub> O <sup>C</sup> OCH <sub>3</sub>	6.0	97
11	CH <sub>2</sub> OH		6.5	96
12	→OH	С С С С С С	5.5	92
13	OH	O O O O C C H <sub>3</sub>	5.0	96
14	F F OH		48	Trace <sup>c</sup>
15	OH	OCH3	6.5	94
16	OH	OCH3	6.5	96

Table	2	(continued )
-------	---	--------------

Entry	Substrate	Product	Time	Yield <sup><math>b</math></sup> (%)
17	OH	O O O O O O C H <sub>3</sub>	12	30 <sup>c</sup>
18	Ph Ph Ph Ph	_	48	_

 $^a$  Reaction conditions: DMC (5 mmol), alcohol (5 mmol), 1 (1 ml) reaction temperature 80  $^\circ \rm C.$   $^b$  Isolated yields.  $^c$  Determined by GC-MS.

into the corresponding methyl carbonates in almost quantitative yields (Table 2, entries 1-4, 13). The reactivity order of alkyl alcohols was primary alcohol > secondary alcohol, which could result mainly from steric hindrance of the alcohols. The aryl alcohols (Table 2, entries 7-12) had lower reactivity than the alkyl ones because of the delocalization of the electrons towards the benzene ring, which probably reduced the nucleophilicity of the alkoxide ion. For the cyclic alcohols (Table 2, entries 5 and 6), the lower reactivity was due to the steric hindrance of the ring. In the case of a more electrophilic alcohol, such as trifluoromethanol, the reaction continued for a longer reaction time (48 h) albeit provided trace yield of the desired product (Table 2, entry 14). Reactions of phenol and its derivatives proceeded smoothly and produced corresponding methyl carbonates in moderate yields (Table 2, entries 15-17). The relatively lower reactivity of the 2,4-dimethyl phenol was considered to be due to its steric effect (Table 2, entry 17). However, no reaction occurred when a tertiary alcohol, such as 1,1,1-triphenyl methanol, was used as the substrate (Table 2, entry 18). The reason why the reaction of 1,1,1-triphenyl methanol did not occur remains unclear. To compare the reactivity of primary and secondary alcohols, a competitive reaction was carried out by using an equimolar mixture of benzyl and cyclohexyl alcohols (10 mmol of each substrate) and DMC (10 mmol) in the presence of 1 (1 ml) as the reaction medium. Both alcohols gave the corresponding methyl carbonates, such as benzyl methyl carbonate and cyclohexyl methyl carbonate, respectively, in 70% and 30% yield (Scheme 3).

Although the exact mechanism of the reaction is not known at this stage, a probable mechanistic pathway for the transesterification of DMC with alcohols is shown in Scheme 4.



Scheme 3 The competitive experiment.



Scheme 4 A possible mechanistic pathway.



The activation of C=O through imidazolium interaction has been well documented in the literature.<sup>25</sup> The nucleophilic addition of alcohol to DMC facilitates the usual pattern of the abstraction of HCl and formation of intermediate **A**. Internal rearrangements of intermediate **A** would produce carbonate ROCO<sub>2</sub>R' and regeneration of the ionic liquid, as shown in Scheme 4. Further, we assume that the acid–base interaction between silicon (electrophile) and the nucleophilic oxygen of the reactant may also be enhancing the reaction rate and is probably responsible for the synergistic effect of the siloxy group in accelerating the rate of the reaction.

Experiments were also carried out to examine the recyclability of the ionic liquid **1** by using 1-hexanol as the substrate. After completion the reaction, the reaction mixture was extracted with diethyl ether to obtain the reaction product. However, the ionic liquid was not dissolved in diethyl ether and therefore was precipitated out and dried under vacuum. The recovered ionic liquid was reused as such for the six subsequent runs (Fig. 1). There was no considerable decrease in the yield of the corresponding carbonate, indicating the efficient recycling of the ionic liquid.

In conclusion, we have demonstrated a simple, efficient and environmentally benign approach for the synthesis of nonsymmetrical organic carbonates *via* the transesterification reaction of alcohols with dimethyl carbonate. The presence of a siloxyl moiety in ionic liquid **1** was found to be beneficial and afforded enhanced reaction rates in terms of product yield and selectivity. The synthesized ionic liquid **1** could be easily recovered and recycled without further purification for subsequent recycling experiments. To the best of our knowledge, this should be the first report concerning the synergistic effect of siloxy group on the reaction rate for organic transformations.

## References

- 1 J. P. Parrish, R. N. Salvatore and K. W. Jung, *Tetrahedron*, 2000, **56**, 8207.
- A. F. Hegarty, *Compr. Org. Chem.*, 1979, 2, 1067; Y. Ono, *Appl. Catal., A*, 1997, 155, 133; M. Pianka, *J. Sci. Food Agric.*, 1966, 17, 47; M. Pianka and P. Sweet, *J. Sci. Food Agric.*, 1968, 19, 667; D. E. Hardies and J. K. Rinehart, *US Pat.*, 4022609, 1970.
- 3 F. Mizia and F. Rivetti, US Pat., 20020056468, 2002;
  B. Schäffner, J. Holz, S. P. Verevkin and A. B. Orner, Chem-SusChem, 2008, 1, 249;
  B. Schäffner, F. Schäffner,
  S. P. Verevkin and A. B. Orner, Chem. Rev., 2010, 110, 4554.
- 4 K. Takamatsu and T. Matsushita, *Jp. Pat.*, 2003277327, 2003; S. Gryglewicz, F. A. Oko and G. Gryglewicz, *Ind. Eng. Chem. Res.*, 2003, **42**, 5007.
- 5 N. Ishida, H. Hasegawa, U. Sasaki and T. Ishikawa, *US Pat.*, 5391311, 1995.
- 6 R. M. Burk and M. B. Roof, *Tetrahedron Lett.*, 1993, 34, 395;
  G. Bertolini, G. Pavich and B. Vergani, *J. Org. Chem.*, 1998, 63, 6031; A. R. Choppin and J. W. Rogers, *J. Am. Chem. Soc.*, 1948, 70, 2967; K. Kondo, N. Sonoda and S. Tsutsumi, *Tetrahedron Lett.*, 1971, 12, 4885; D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, 1974, 39, 701; A. A. G. Shaikh and S. Siviram, *Chem. Rev.*, 1996, 96, 951; L. Cotarca, P. Delogu, A. Nardelli and V. Sunjic, *Synthesis*, 1996, 553.
- 7 (a) Y. Kishimoto and I. Ogawa, *Ind. Eng. Chem. Res.*, 2004,
  43, 8155; (b) B. M. Bhanage, S. I. Fujita, Y. Ikushima, K. Torii and M. Arai, *Green Chem.*, 2003, 5, 71; (c) Y. H. Chang, T. Jiang, B. X. Han, Z. M. Liu, W. Z. Wu, L. Gao, J. C. Li, H. X. Gao, G. Y. Zhao and J. Huang, *Appl. Catal.*, A, 2004, 263, 179; (d) J.-S. Tian, C.-X. Miao, J.-Q. Wang, F. Cai, Y. Du, Y. Zhao and L.-N. He, *Green Chem.*, 2007, 9, 566.
- 8 S. Fujita, B. M. Bhanage, Y. Ikushima and M. Arai, *Green Chem.*, 2001, **3**, 87.
- 9 M. A. Casadei, S. Cesa and L. Rossi, *Eur. J. Org. Chem.*, 2000, 2445; L. Zhang, D. Niu, K. Zhang, G. Zhang, Y. Luo and J. Lu, *Green Chem.*, 2008, **10**, 202.
- S. I. Kim, F. Chu, E. E. Dueno and K. W. Jung, *J. Org. Chem.*, 1999, **64**, 4578; R. N. Salvatore, V. L. Flanders, D. Ha and K. W. Jung, *Org. Lett.*, 2000, **2**, 2797.
- 11 M. O. Bratt and P. C. Taylor, J. Org. Chem., 2003, 68, 5439.
- 12 Y. R. Jorapur and D. Y. Chi, J. Org. Chem., 2005, 70, 10774.
- 13 J. Song, B. Zhang, T. Wu, G. Yang and B. Han, *Green Chem.*, 2011, 13, 922.
- 14 A. A. G. Shaikh and S. Sivaram, Chem. Rev., 1996, 96, 951.

- 15 J. Song and B. Han, *Green Chem.*, 2011, **13**, 922; H. Mutlu and M. A. R. Meier, *Green Chem.*, 2012, **14**, 1728.
- 16 S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori and R. Sartorio, *J. Catal.*, 2002, **205**, 199.
- 17 B. Veldurthy and F. Figueras, Chem. Commun., 2004, 734.
- 18 B. Veldurthy, J. M. Clacens and F. Figueras, *Eur. J. Org. Chem.*, 2005, 1972.
- 19 M. L. Kantam, U. Pal, B. Sreedhar and B. M. Choudary, *Adv. Synth. Catal.*, 2007, **349**, 1671.
- 20 Y. X. Zhou, S. G. Liang, J. L. Song, T. B. Wu, S. Q. Hu, H. Z. Liuand and B. X. Han, *Acta Phys.-Chim. Sin.*, 2010, **26**, 1.
- 21 H. Noda, K. Motokura, A. Miyaji and T. Baba, *Angew. Chem., Int. Ed.*, 2012, **51**, 1.
- 22 P. U. Naik, L. Petitjean, K. Refes, M. Picquet and L. Plasserauda, *Adv. Synth. Catal.*, 2009, **351**, 1753.

- 23 M. Selva, M. Noè, A. Perosa and M. Gottardo, Org. Biomol. Chem., 2012, 10, 6569.
- 24 (a) H. Valizadeh, M. Amiri, A. Shomali and F. Hosseinzadeh, J. Iran. Chem. Soc., 2011, 8, 495–501; (b) V. Blasucci, C. Dilek, H. Huttenhower, E. John, V. L. Mestre, P. Pollet, C. A. Eckert and C. L. Liotta, Chem. Commun., 2009, 116.
- 25 (a) V. Maria de Oliveira, R. Silva de Jesus, A. F. Gomes, F. C. Gozzo, A. P. Umpierre, P. A. Z. Suarez, J. C. Rubim and B. A. D. Neto, *ChemCatChem*, 2011, 3, 1911; (b) L. S. Santos, B. A. D. Neto, C. S. Consorti, C. H. Pavam, W. P. Almeida, F. Coelho, J. Dupont and M. N. Eberlin, *J. Phys. Org. Chem.*, 2006, 19, 731; (c) L. M. Ramos, B. C. Guido, C. C. Nobrega, J. R. Correa, R. G. Silva, H. C. B. de Oliveira, A. F. Gomes, F. C. Gozzo and B. A. D. Neto, *Chem.-Eur. J.*, 2013, 19, 4156.