ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: Chem. Commun., 2016, 52, 10787

Received 12th July 2016,
Accepted 8th August 2016

DOI: 10.1039/c6cc05730f

www.rsc.org/chemcomm

Synthesis of cyclic carbonates from diols and CO_2 catalyzed by carbenes†

Felix D. Bobbink,‡ Weronika Gruszka,‡ Martin Hulla, Shoubhik Das and Paul J. Dyson*

The synthesis of cyclic carbonates from epoxides and CO_2 is a well-established reaction, whereas the synthesis of cyclic carbonates from diols and CO_2 is considerably more challenging, and few efficient catalysts are available. Here, we describe heterocyclic carbene catalysts, including one derived from a cheap and efficient thiazolium salt, for this latter reaction. The reaction proceeds at atmospheric pressure in the presence of an alkyl halide and Cs_2CO_3. Reaction mechanisms for the transformations involved are also proposed.

Utilization of carbon dioxide (CO_2) in the production of fine chemicals and synthetic fuels would contribute towards a more sustainable chemical industry. However, CO_2 is a challenging molecule to activate as it is thermodynamically stable and kinetically inert in many transformations. Accordingly, only a few energy-efficient processes which employ CO_2 have been commercialized.[1]

From a thermodynamic perspective, oxygenated cyclic carbonates are particularly suitable synthetic targets from CO_2. These compounds have been exploited as electrolytes for lithium ion batteries,[2] building blocks for polymeric materials,[3,4] solvents[5,6] and intermediates in the synthesis of compounds such as dimethyl carbonate (DMC)[7] and ethylene glycol.[8] Industrial production of cyclic carbonates involves either the transesterification of diols with phosgene in an energy-intensive process[9] or the cycloaddition of CO_2 to epoxides.[10–12] Despite the latter route exhibiting 100% atom economy and industrial scalability, the synthesis of epoxides combined with their high reactivity and volatility are problematic. Recently, more stable, biodegradable 1,2-diols have been proposed as promising alternatives for the synthesis of cyclic carbonates with CO_2.[13] Their reaction with CO_2 is, however, neither kinetically nor thermodynamically-favored due to the formation of water as the sole by-product.[14] Attempts have been made to by-pass this problem by the implementation of a suitable catalyst system and a dehydrating agent. Both heterogeneous and homogeneous catalysts have been proposed for this reaction. For example, a heterogeneous cascade catalysis comprising CeO_2 and 2-cyanopyridine is arguably the most efficient system.[15] However, this process requires harsh reaction conditions (150 °C and 50 bars of CO_2), an expensive reagent (2-cyanopyridine) and the activity is highly sensitive to the size of ceria particles. A number of homogeneous metal-free catalysts run under milder conditions and, interestingly, all are based on the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) aided insertion of CO_2. Different reagents are used to facilitate the subsequent alkylation step to afford cyclic carbonates in good yield under only 10 bars of CO_2.[16] The reaction may even proceed at an atmospheric pressure of CO_2 if DBU and the alkyl halide are used in large excess.[17] The same mild conditions are employed in a system in which tosyl chloride and triethylamine are used to afford cyclic carbonates with 6-membered rings in good yields.[18] Ultimately, only a few efficient processes exist and finding an increasingly sustainable process for this reaction remains important.

Recently, N-heterocyclic carbenes (NHCs) have gained interest as catalysts for reactions which employ CO_2 as a substrate.[19–23] This stems from their ability to act as nucleophiles which activate CO_2 *via* the formation of imidazolium carboxylates.[24,25] Interestingly, these intermediates have been previously reported to catalyze the synthesis of cyclic carbonates from diols employing DMC as the carbonyl source rather than CO_2.[26] Herein, we show the utility of carbene catalysts for the synthesis of cyclic carbonates from diols and CO_2 and, based on key experiments, propose plausible mechanisms for this transformation.

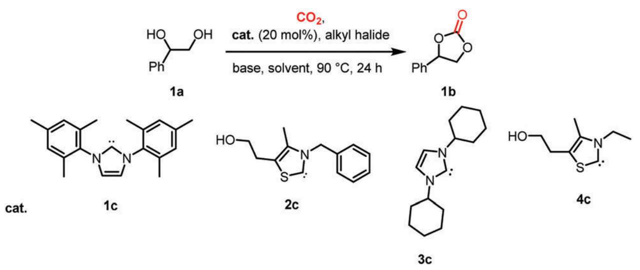
Initially, reaction conditions were optimized using 1-phenyl-1,2-ethanediol (**1a**) as the substrate, see Table 1. Several imidazolium and thiazolium carbene catalysts (**1c**–**4c**) were evaluated. NHCs **1c** and **3c**[19] and the thiazolium carbene catalysts **1b** and **1d**[27] have been previously shown to catalyze the *N*-methylation of amines using CO_2 as the carbon source. The efficiency of a variety of bases and alkyl halides was also studied as they are essential for the reaction to proceed (see below).[16,18]

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. E-mail: paul.dyson@epfl.ch

† Electronic supplementary information (ESI) available: Full experimental and spectroscopy data. See DOI: 10.1039/c6cc05730f

‡ The authors contributed equally to this work.

Table 1 Optimization of the reaction conditions for the transformation of 1-phenyl-1,2-ethanediol (**1a**) used as a model substrate



Entry	Catalyst	Alkyl halide (eq.)	Base (eq.)	Yield (%)
1	**1c**[a]	CH_2Br_2 (2)	Cs_2CO_3 (2)	44
2	**2c**[a]	CH_2Br_2 (2)	Cs_2CO_3 (2)	45
3	**3c**[a]	CH_2Br_2 (2)	Cs_2CO_3 (2)	29
4	**4c**[a]	CH_2Br_2 (2)	Cs_2CO_3 (2)	32
5	**1c**[a]	CH_2Br_2 (5)	Cs_2CO_3 (2)	42
6	**2c**[a]	CH_2Br_2 (5)	Cs_2CO_3 (2)	61
7	**2c**[a]	CH_2Br_2 (5)	Cs_2CO_3 (3)	53
8	**2c**	CH_2Br_2 (5)	Cs_2CO_3 (3)	71
9	**2c**	CH_2Br_2 (5)	Na_2CO_3 (3)	0
10	**2c**	CH_2Br_2 (5)	K_2CO_3 (3)	5
11	**2c**	CH_2Br_2 (5)	DBU (3)	21
12	**2c**	CH_2Br_2 (5)	Et_3N (3)	0
13 (50 °C)	**2c**	CH_2Br_2 (5)	Cs_2CO_3 (3)	5
14 (70 °C)	**2c**	CH_2Br_2 (5)	Cs_2CO_3 (3)	12
15 (110 °C)	**2c**	CH_2Br_2 (5)	Cs_2CO_3 (3)	25
16	**2c**	$(CH_2Br)_2$ (5)	Cs_2CO_3 (3)	37
17	**2c**	$(C_2H_4Br)_2$ (5)	Cs_2CO_3 (3)	32
18	**2c**	C_4H_9Br (5)	Cs_2CO_3 (3)	59
19	**2c**	C_4H_9Cl (5)	Cs_2CO_3 (3)	20
20	**2c**	**C_4H_9Br (2)**	**Cs_2CO_3 (3)**	**81**
21 (DMSO)	**2c**	C_4H_9Br (2)	Cs_2CO_3 (3)	33
22 (DMA)	**2c**	C_4H_9Br (2)	Cs_2CO_3 (3)	50
23 (Toluene)	**2c**	C_4H_9Br (2)	Cs_2CO_3 (3)	0

Reaction conditions: **1a** (0.5 mmol), catalyst (20 mol%), alkyl halide (1–2.5 mmol), base (1–1.5 mmol), DMF (4 mL), CO_2 (1 atm). Yields were determined by GC-FID using *n*-decane as internal standard. [a] The carbene catalyst was generated with NaH. Otherwise, the carbene is generated *in situ* using an extra 20 mol% base.

The ability of cesium carbonate (Cs_2CO_3) to activate CO_2 and other small molecules[28–32] encouraged us to employ it as a base in the reaction. Dibromomethane (CH_2Br_2) was also used due its efficiency in forming an effective leaving group.[16] The activity of **1c**–**4c** was investigated in the presence of 2 eq. of CH_2Br_2 and 2 eq. of Cs_2CO_3. The highest yields of styrene carbonate (**1b**) were obtained with catalysts **1c** and **2c** (Table 1, entries 1 and 2). In contrast, **3c** and **4c** resulted in lower product yields (Table 1, entries 3 and 4). The effect of quantities of CH_2Br_2 and Cs_2CO_3 on the reaction was studied. Increasing CH_2Br_2 to 5 eq. resulted in 61% yield of styrene carbonate **1b** (Table 1, entry 6). Interestingly, a larger excess of the base (3 eq. instead of 2 eq.) led to a slight decrease in the yield of **1b** (Table 1, entry 7). It should be noted that the reaction proceeds in low yield using Cs_2CO_3 as the base in the absence of CO_2 (Table S2, entry 2, ESI†). However, ^{13}C labeled CO_2 was used to confirm that the main source of the carbonyl group incorporated in the cyclic carbonate product originates from CO_2 (see NMR spectra comparing the ^{13}C NMR spectra of non-labeled and ^{13}C labeled products in the ESI†).

The enhanced activity of catalyst **2c** might be due to a greater stability to moisture; note that **1b** was not observed in a control experiment in which water was introduced into the system (Table S2, entry 6, ESI†). In the initial catalytic runs the active carbene catalyst was generated prior to reaction by the deprotonation of the corresponding salt with NaH. Subsequently, we found that the *in situ* generation of the carbene catalyst yielded **1b** in 71% in presence of 3 eq. of Cs_2CO_3 (Table 1, entry 8). Interestingly, in a previous study using the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[bmim][PF_6]$) as solvent, the increased carbonate yield was attributed to the increased solubility of CO_2.[16] Presumably, an active carbene was also generated by the deprotonation of the imidazolium salt by DBU – the ability of DBU and Cs_2CO_3 to deprotonate $[bmim][BF_4]$ to form a NHC has been reported.[33] DBU was evaluated under our conditions, but yielded **1b** in a significantly lower yield (Table 1, entry 11).[16] Na_2CO_3 and K_2CO_3 were evaluated in place of Cs_2CO_3, but afford the product in 0 and 5% yield, respectively, presumably due to the lower solubility of these carbonates in DMF (Table 1, entries 9 and 10). No product was observed with Et_3N (Table 1, entry 12). We speculate that Et_3N, which is often employed in the Stetter reaction, may undergo a Menshutkin reaction with CH_2Br_2 thereby inhibiting the reaction. Notably, Cs_2CO_3 was found to be the optimal base in this reaction owing to its ability to generate the active carbene catalyst as well as to act as a minor carbonyl donor and a dehydrating agent.

Dimethylformamide (DMF) was selected as a reaction solvent as it can activate CO_2.[34] As expected, other polar aprotic solvents (dimethyl sulfoxide (DMSO) or dimethylacetamide (DMA)) could also be used (Table 1, entries 21 and 22), whereas no reaction was observed in toluene (Table 1, entry 23).

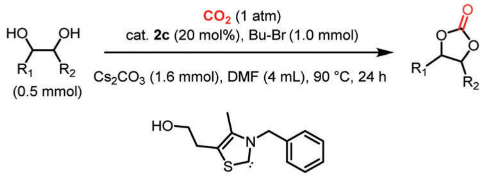
The optimum reaction temperature is 90 °C, with lower temperatures leading to a decrease in product yield (Table 1, entries 13 and 14) and with more elevated temperatures, *e.g.* 110 °C, leading to deactivation of the catalytic system (Table 1, entry 15). The alkyl halide also affects the reaction, in particular, 2 eq. of bromobutane (C_4H_9Br) results in a higher yield than 5 eq. of CH_2Br_2 (Table 1, entries 8 and 20). The other alkyl halides evaluated were less effective (Table 1, entries 16, 17 and 19).

Based on the optimized conditions, which afford **1b** in up to 81% yield, the scope of the reaction was explored using catalyst **2c** (Table 2). The substrates varied from 1,2-diols to 1,3-diols (**2a**–**4a**) bearing functional groups with varying steric influence. The diols were subjected to the optimized conditions of 2 eq. bromobutane, 3.2 eq. Cs_2CO_3 at 90 °C and 1 atm CO_2 pressure.

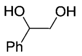
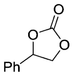
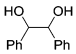
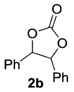
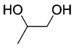
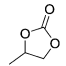
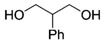
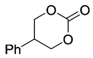
The model product 4-phenyl-1,3-dioxolan-2-one was isolated in 61% yield (Table 2, entry 1). Five-membered cyclic carbonates, 4,5-diphenyl-1,3-dioxolan-2-one (**2b**) and propylene carbonate (**3b**) were obtained in yields of 63 and 54%, respectively (Table 2, entries 2 and 3). The six-membered cyclic carbonate, 5-phenyl-1,3-dioxan-2-one (**4b**) was produced in 53% (Table 2, entry 4). These yields are comparable to those obtained using alternative methods (see Table S1, ESI† for a comparison).[16,17]

On the basis of our results and previous literature, two plausible reaction mechanisms in Schemes 1 and 2 are suggested.[16,26,35,36]

Table 2 Reaction of various diols with CO_2 under optimized conditions

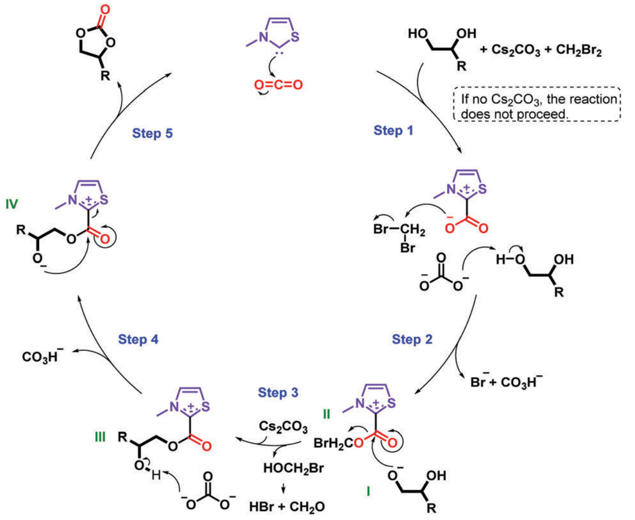


cat. **2c**

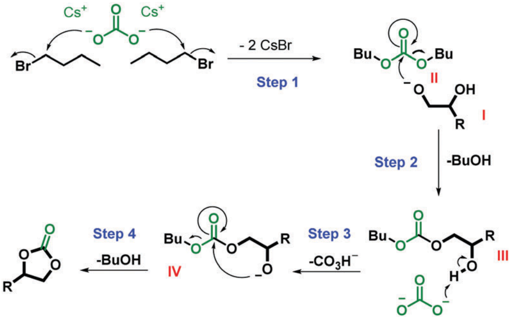
Entry	Reactant	Product	Yield (%)
1	 **1a**	 **1b**	61[a]
2	 **2a**	 **2b**	63[a]
3	 **3a**	 **3b**	54[b]
4	 **4a**	 **4b**	53[b]

Reaction conditions: substrate (0.5 mmol), cat. **2c** (20 mol%), C_4H_9Br (1.0 mmol), Cs_2CO_3 (1.6 mmol), DMF (4 mL), CO_2 (1 atm), 24 h, 90 °C. [a] Isolated yield. [b] GC yield.

Scheme 1 presents the principal mechanism for the carbene-catalyzed reaction. As mentioned above, both the base and alkyl halide are essential in the reaction, as confirmed in control experiments in which no carbonate was formed in their absence (Table S1, entries 4 and 5, ESI†). Scheme 2 represents the mechanism for the minor non-catalytic formation of cyclic carbonate in the absence of CO_2 (Table S1, entry 2, ESI†). C_4H_9Br is included in the second mechanism due to detection of dibutyl carbonate and *n*-butanol in the reaction mixture using GC-MS, see ESI.† However, a similar mechanism is likely to take place in presence of other alkyl halides. Moreover, both of these mechanisms appear to occur concurrently to form the cyclic carbonate. This hypothesis is based on our finding that while 25% of **1b** was obtained in the absence of CO_2 (Table S1, entry 2, ESI†), addition of CO_2 increased the yield of **1b** to 81% (Table 1, entry 17).



Scheme 1 Tentative mechanism for the carbene-catalyzed reaction of diols and CO_2 to form cyclic carbonates. The substituents of the catalyst are omitted for clarity.



Scheme 2 Proposed mechanism for the non-catalytic reaction of diols and CO_2 to form cyclic carbonates.

In the mechanism in Scheme 1, step 2 involves the generation of an alkoxide **I** and the parallel attack of the carbene–CO_2 adduct on CH_2Br_2 after activation of CO_2 by the carbene in step 1. Nucleophilic attack of the alkoxide **I** on intermediate **II** in step 3 results in the elimination of the leaving group and formation of intermediate **III**. In step 4, the secondary hydroxyl group of the diol is deprotonated, leading to the generation of intermediate **IV** and, in the final step (step 5), the intramolecular addition of the alcohol occurs in intermediate **IV**, which affords the cyclic carbonate and regenerates the catalyst. Notably, bromomethanol is eliminated as a leaving group, however bromomethanol is unstable, and hence it is believed to decompose to a mixture of hydrogen bromide (HBr) and formaldehyde (CH_2O).[37] Note, the formation of these side-products was not detected by spectroscopic or chromatographic studies, possibly due to neutralization of HBr by Cs_2CO_3 and the volatility of CH_2O.

The secondary (non-catalytic) reaction in Scheme 2 proceeds by the attack of Cs_2CO_3 on C_4H_9Br in step 1, leading to the formation of intermediate **II** (dibutyl carbonate was observed by GC-MS). Similar to the mechanism in Scheme 1, the reaction of the alkoxide **I** with intermediate **II** in step 2 leads to the elimination of butanol (observed by GC-MS) and the formation of intermediate **III**. Again, the deprotonation of the secondary hydroxyl group in intermediate **III** in step 3 results in the formation of intermediate **IV**. The final cyclization in step 4 leads to the elimination of the second leaving group and the formation of the cyclic carbonate.

In summary, the work presented here offers an approach for the synthesis of cyclic carbonates from diols and CO_2. The proposed system benefits from the use of environmentally-friendly metal-free carbene catalysts. Using this methodology cyclic carbonates were obtained under mild conditions (90 °C and atmospheric pressure of CO_2) in good yield and comparable or better to those obtained with other catalysts that operate under more forcing conditions. Based on labelling studies and other experiments two-mechanisms are proposed, one non-catalytic and one catalytic that account for the overall reaction.

The EPFL, the CTI Swiss Competence Center of Energy Research (SCCER) on Heat and Electricity Storage and the Fondation Claude et Juliana are thanked for funding.

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