Green Chemistry

RSC Publishing

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View Journal

Synthesis of cyclic carbonates with carbon dioxide and cesium carbonate

Cite this: DOI: 10.1039/c3gc40790j

Received 26th April 2013,
Accepted 2nd June 2013

DOI: 10.1039/c3gc40790j

www.rsc.org/greenchem

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Cyclic carbonates are important compounds for the synthesis of biocompatible polymers and linear dialkyl carbonates, as well as solvents and electrolytes. We report here the synthesis of such compounds from easily accessible starting materials with carbon dioxide as a C1 source and caesium carbonate as the base. This new methodology is able to yield 5- and 6-membered cyclic carbonates very efficiently in a green manner.

Introduction

In recent years, cyclic carbonates have attracted increasing attention as a versatile monomer for the synthesis of biocompatible polymers,[1] as polar aprotic solvents and degreaser,[2] as electrolytes and as intermediates for linear dialkyl carbonate synthesis.[3] In light of increased interest in biocompatible materials, the synthesis of cyclic carbonates in a safe, reliable and environmentally benign way has become important. Traditionally, cyclic carbonates are synthesized by the reaction of phosgene or the coupling of halo formates with diols.[4] However, these methods involving toxic materials are not environmentally satisfactory. Recent developments have aimed to replace phosgene with the relatively safer triphosgene or oxalylchoride.[5] Several novel synthetic strategies for the synthesis of cyclic carbonates were also developed recently which include carbon dioxide insertion in epoxides[2,4,6] and oxetane,[7] transesterification of diols with urea[8] and oxidative carbonylation of diols using carbon monoxide, with the aid of a transition metal catalyst,[9] and catalytic reaction from specific precursors such as propargyl alcohols.[10] However, these methods still rely on specific precursors and have limited substrate scope.

The use of carbon dioxide for the formation of cyclic carbonates has been very successfully employed for the conversion of epoxides into ethylene carbonate (EC) analogs.[2,4,6,11] However, the reaction is quite limited in the substrate scope, and only 5-membered cyclic carbonates can be obtained. When oxetane is used, trimethyl carbonate (TMC) analogs can be obtained; again, the substrate scope is very limited.[12] As a result, the methodology has less impact on the modern synthetic laboratory. Obviously, the simultaneous conversion of CO_2 and diols into cyclic carbonates is highly desirable, in which water is the only byproduct and the process is highly atom-efficient. However, this ideal reaction is both thermodynamically and kinetically not favored.[13] Some heterogeneous and homogeneous catalysts have been developed to accelerate this reaction. However, the overall conversion of diols is very low (~5%).[14] The limiting factor for this chemical equilibrium is the water by-product; accordingly, dehydrating agents, such as triphenylphosphine–diethyl azodicarboxylate, were introduced into this reaction system but the efficiency of the reaction was still unsatisfactory.[14,15] Furthermore, this methodology was only successful in the synthesis of ethylene carbonates. Alternatively, halohydrin has also been used in the synthesis of ethylene carbonates and related five-membered cyclic carbonates under catalytic and pressurized conditions.[16] Although methods have also been developed for the synthesis of organic carbonates by using alkyl halides and alcohols, this protocol has never been used for the synthesis of any cyclic carbonates other than ethylene carbonates.[17]

We have been interested in utilizing carbon dioxide as a feedstock for organic synthesis over the last few years.[18] However, the activation and reaction of carbon dioxide under mild conditions still remains a challenge in synthetic organic chemistry. Here, we report a convenient and robust method for the synthesis of 5- and 6-membered cyclic carbonates from commercially available and easily accessible starting materials using mild reaction conditions. The intermolecular ring closing reaction proceeds in the presence of 1 atm CO_2 and Cs_2CO_3 very efficiently, thus providing an environmentally benign method for the synthesis of cyclic carbonates.

Results and discussion

In our initial efforts to synthesize cyclic carbonates in a green manner without the use of a transition metal catalyst, we used

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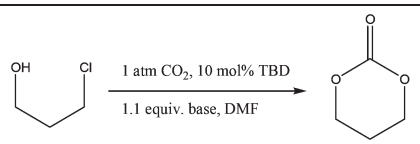
the more general halo-alcohols as starting materials. The potential problem here is the production of a large amount of polycarbonate with low selectivity for the desired cyclic carbonate.[17] In our initial study, the reaction was carried out with 3-chloro-1-propanol and CO_2 in the presence of K_2CO_3 and a catalytic amount of triazabicyclodecene (TBD) (Table 1) in DMF. At 60 °C, trimethyl carbonate (TMC, compound **1**) could be detected in 58% yield by NMR spectroscopy, whereas a small decrease in yield was observed when the reaction was carried out at 40 °C. Interestingly, we only observed minor polymeric side products of compound **1** even though TBD was used as an additive.[19] It has to be mentioned here that even sparteine, a weaker base than TBD, is able to polymerize TMC in minutes.[20] This is the first example demonstrating that a 6-membered cyclic carbonate can be synthesized directly from CO_2 without using any transition metal or toxic agents, such as phosgene or CO.[4,9] We do believe that the CO_2 present in the reaction is able to act as an inhibitor by binding to TBD, thus preventing the polymerization of the newly formed compound **1**.

An increase in the yield of compound **1** was observed when K_2CO_3 was replaced with Cs_2CO_3. At 60 °C, compound **1** was formed with up to 77% NMR yield, whereas almost quantitative formation of compound **1** was detected by lowering the temperature to 40 °C. However, employing the stronger base KO^{t}Bu resulted in a significant decrease in yield and only 20% of compound **1** could be detected by NMR.

Table 1 Influence of the base on TMC formation



Entry	Base	T/°C	Yield[a]/%
1	K_2CO_3	60	58
2	K_2CO_3	40	54
3	Cs_2CO_3	60	77
4	Cs_2CO_3	40	95
5	KO^{t}Bu	40	20
6[b]	Cs_2CO_3	40	95

[a] Yield was determined by ^{1}H-NMR using mesitylene as the internal standard. [b] No TBD added.

We further looked at the influence of the catalyst on the reaction and, thus, we replaced TBD with imidazolium based catalysts to activate CO_2.[21] When 1,3-(2,6-diisopropylphenyl)-imidazolium (IPr) was used, no change in yield was observed; however, the use of 1,3-(2,6-dimethylphenyl)-imidazolinimum (SMes) resulted in a slight decrease in yield (92%).

Since only minor changes in the yield were observed with different catalysts but large changes in the yield were observed with different bases, the role of the catalyst in the reaction was further investigated. When standard conditions were applied (40 °C, 1 atm CO_2, 1.1 equiv. Cs_2CO_3, 15 h reaction time) in the absence of a catalyst, the same NMR yield (95%) of compound **1** was observed. We therefore concluded that the addition of a catalyst for the activation of CO_2 is not needed in order to form TMC.

Furthermore, the role of Cs_2CO_3 was investigated. When a substoichiometric amount of Cs_2CO_3 was used, incomplete conversion was observed. Instead, the yield of compound **1** correlated with the amount of Cs_2CO_3 used, which indicates that Cs_2CO_3 does not act as a catalyst in this reaction.

In order to prove that CO_2 is essential for the reaction, we carried out the experiment in the absence of CO_2. As expected, compound **1** could not be observed after the reaction was quenched. Other polar volatile solvents, namely THF and acetonitrile, were also tested, but no successful reaction could be observed. In addition, when the reaction was performed using water as a solvent, no product could be detected.

Based on the above results, we postulate the following reaction mechanism (Fig. 1). In the initial step, Cs_2CO_3 deprotonates the alcohol, resulting in the formation of cesium alkoxide, which subsequently reacts with CO_2 to form a carbonate. In the final step, TMC is formed by an intramolecular ring closing reaction, affording CsCl as the side product.[17] To prove our postulated reaction mechanism and the formation of CsCl, we performed a reaction using a substoichiometric amount of Cs_2CO_3 and collected the solids after 15 h reaction time. To verify the presence of Cl^-, a small amount of solid was dissolved in water and nitric acid was added to remove residual Cs_2CO_3. The test for Cl^- was positive using $AgNO_3$ for qualitative verification.

The substrate scope of the reaction was then investigated. We first looked into changing the chloride to other halides; 2-bromo-1-ethanol as well as 2-iodo-1-ethanol afforded the expected product **2** in 92% yield by NMR spectroscopy. Since

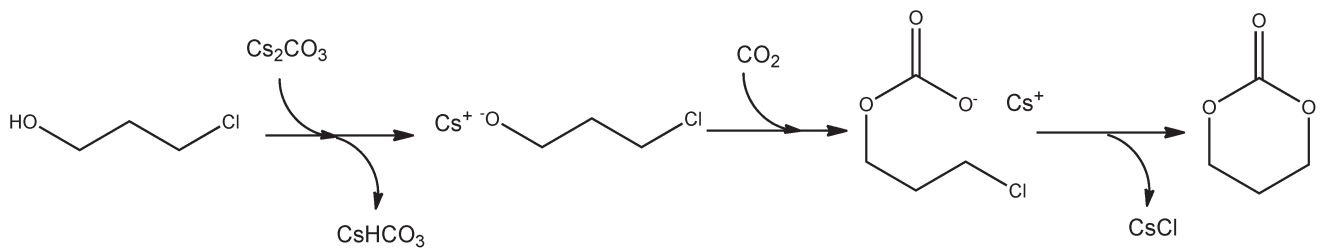


Fig. 1 Proposed reaction mechanism for the formation of TMC using 3-chloro-1-propanol as the starting material and Cs_2CO_3 as the base.

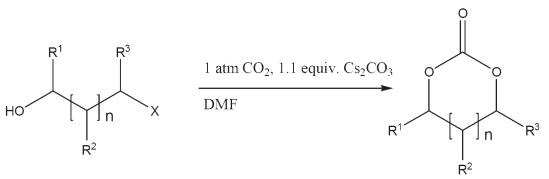
the accessibility of halide alcohols is limited, the possibility of using tosylate as the leaving group was explored. Tosylates are very easily accessible by reaction of tosyl chloride with the respective alcohols in the presence of a base. This synthetic strategy would allow the conversion of diols in two reaction steps into cyclic carbonates.

Reaction of 2-tosyl-1-ethanol with CO_2 in the presence of 1.1 equivalents of Cs_2CO_3 in DMF yielded ethylene carbonate in comparable yield to the product obtained from 2-bromo-1-ethanol. The selectivity of the reaction to form five-membered rings over six-membered rings was also investigated using (±)-3-chloro-1,2-propanediol. After 15 h reaction time, (±)-3-chloro-1,2-propanediol was converted exclusively into glyceryl carbonate (**3**), a versatile chemical.[22] The exclusive formation of the five-membered ring demonstrates the high selectivity of the reaction to yield the thermodynamically more stable compound.

To further expand the substrate scope, we looked into the possibility of forming 7- and 8-membered rings. When 4-chlorobutan-1-ol was reacted with CO_2 in the presence of 1.1 equivalents of Cs_2CO_3 in DMF, no product could be observed by ^{1}H and ^{13}C NMR spectroscopy. The same holds true when 5-bromopentan-1-ol was used as the starting material. This is not unexpected taking into account that 7- and 8-membered rings are kinetically not favored. In addition, the C═O bond distorts the ring which most likely decreases the thermodynamic stability.

A number of substrates yielding 5- and 6-membered rings were screened and the results are shown in Table 2. Residues R^1, R^2 and R^3 were either a methyl, a phenyl or a CH_2OH group respectively. While no significant difference in yield was observed when only one residue was substituted, a slight drop in yield could be detected when R^1 and R^3 were a methyl group. This may be attributed to steric hindrance as well as a decrease in nucleophilicity. In general, both 5- and 6-membered rings could be formed in moderate to excellent yield.

Table 2 Scope of cyclic carbonate formation with CO_2



Compound	X	*n*	R^1	R^2	R^3	Yield [%]
1	Cl	1	H	H	H	95
2	Br	0	H	N.A.	H	75
3	Cl	0	CH_2OH	N.A.	H	92
4	OTs	0	Ph	N.A.	H	77
5	OTs	1	H	$(CH_3)_2$	H	71
6	OTs	1	Me	H	Me	65
7	OTs	1	H	Ph	H	95

Experimental section

All reactions were set up in an Innovative Technologies Glovebox equipped with nitrogen gas. Chemicals were purchased from commercial sources and used as received without further purification. Anhydrous solvents were purchased in Sure-seal packaging from Sigma-Aldrich and were used as received. CO_2 was supplied by SOXAL. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz) instrument. Reaction temperatures refer to the temperatures of the heating blocks. Mono-tosylated diols were synthesised according to previously reported standard tosylation reaction conditions.[23] With the exception of compound **7**, all cyclic carbonates reported herein have been previously prepared by other methods and characterized by NMR spectroscopy: 1,3-dioxan-2-one (**1**),[24] ethylene carbonate (**2**),[5,24a] 4-(hydroxymethyl)-1,3-dioxolan-2-one (**3**),[9,25] 4-phenyl-1,3-dioxolan-2-one (**4**),[26] 5,5-dimethyl-1,3-dioxan-2-one (**5**),[24a] and 4,6-dimethyl-1,3-dioxan-2-one (**6**).[27]

General reaction procedure

In a nitrogen filled glove box, a 20 mL crimp top vial was charged with 1 mmol starting material and dissolved in 3 mL DMF; 1.1 mmol (1.1. equiv.) Cs_2CO_3 was then added immediately. The vial was closed with a crimp cap, brought out of the glove box and CO_2 was bubbled through the solution for about 1 minute. The vial was placed on a 40 °C heat block and stirred for 15 h under 1 atm of CO_2 using a CO_2 filled balloon. The reaction was quenched by adding 15 mL DCM. The resulting suspension was filtered over Celite; the solvent was first removed on a rotary evaporator and DMF was later on removed on an oil vacuum pump. After 6 h, the residue was resuspended in DCM and filtered over cotton wool to remove all salt traces. The solvent was removed and the product was dried on an oil vacuum pump.

1,3-Dioxan-2-one (1). Yield: 95%; ^{1}H-NMR ($CDCl_3$): δ = 4.45 (t, 4H, $^3J_{HH}$ = 5.8 Hz, O–CH_2), 2.14 (quintet, 2H, $^3J_{HH}$ = 5.8 Hz, CH_2) ppm; ^{13}C-NMR ($CDCl_3$): δ = 148.5 (C═O), 68.1 (O–CH_2), 21.8 (CH_2) ppm.

Ethylene carbonate (2). Yield: 75%; ^{1}H-NMR ($CDCl_3$): δ = 4.48 (s, 4H, CH_2) ppm; ^{13}C-NMR ($CDCl_3$): 155.7 (C═O), 64.8 (CH_2) ppm.

4-(Hydroxymethyl)-1,3-dioxolan-2-one (3). Yield: 92%; ^{1}H-NMR ($CDCl_3$): δ = 4.81 (m, 1H), 4.55–4.43 (m, 2H), 3.98 (dd, 1H, $^3J_{HH}$ = 12.9 Hz, $^2J_{HH}$ = 3.0 Hz), 3.71 (dd, 1H, $^3J_{HH}$ = 12.9 Hz, $^2J_{HH}$ = 3.4 Hz), 2.40 (bs, 1H, O*H*) ppm; ^{13}C-NMR ($CDCl_3$): δ = 155.5 (*C*═O), 76.8 (*C*H), 65.9 (*C*H_2), 61.8 (*C*H_2) ppm.

4-Phenyl-1,3-dioxolan-2-one (4). Yield: 76%; ^{1}H-NMR ($CDCl_3$): δ = 7.49–7.41 (m, 3H, Ph), 7.39–7.34 (m, 2H, Ph), 5.66 (t, 1H, $^3J_{HH}$ = 8.0 Hz, C*H*), 4.80 (t, 1H, $^3J_{HH}$ = 8.4 Hz, CH_2), 4.35 (t, 1H, $^3J_{HH}$ = 8.4 Hz, CH_2) ppm; ^{13}C-NMR ($CDCl_3$): δ = 154.9 (C═O), 136.0 (C_q), 129.9 (CH, Ph), 129.4 (CH, Ph), 126.0 (CH, Ph), 78.1 (CH–Ph), 71.3 (CH_2) ppm.

5,5-Dimethyl-1,3-dioxan-2-one (5). Yield: 71%; ^{1}H-NMR ($CDCl_3$): δ = 4.07 (s, 4H, CH_2), 1.12 (s, 6H, CH_3) ppm; ^{13}C-NMR

($CDCl_3$): δ = 148.4 (C═O), 77.6 (CH_2), 28.6 ($C(CH_3)_2$), 21.3 (CH_3) ppm.

4,6-Dimethyl-1,3-dioxan-2-one (6). Yield: 65%; ^{1}H-NMR ($CDCl_3$): δ = 4.53 (m, 2H), 2.04 (m, 1H), 1.54 (m, 1H), 1.34 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 149.6 (*C*═O), 75.4 (*C*H), 36.4 (*C*H_2), 21.2 (*C*H_3) ppm.

5-Phenyl-1,3-dioxan-2-one (7). Yield: 95%; ^{1}H-NMR ($CDCl_3$): δ = 7.42–7.31 (m, 3H, Ph), 7.23 (m, 2H, Ph), 4.61–4.49 (m, 4H, O–CH_2), 3.49 (m, 1H, C*H*) ppm; ^{13}C ($CDCl_3$): δ = 148.3 (*C*═O), 134.2 (CH–*C*), 129.5 (CH on bottom), 128.7 (CH in the middle), 127.6 (CH on the top next to Cq), 72.2 (O–*C*H_2), 37.7 (*C*H) ppm.

Conclusions

In conclusion, a new method for the green synthesis of cyclic carbonates is presented. This novel synthetic approach does not require any transition metal or organo catalyst; only Cs_2CO_3 base and CO_2 are required. The reaction proceeds very efficiently at 40 °C under 1 atm CO_2, yielding 5- and 6-membered cyclic carbonates in good to excellent yield. We could further prove that the reaction is very robust, yielding the expected product when chloride, bromide, iodide or tosyl is used as the leaving group.

Acknowledgements

This work was funded by the Institute of Bioengineering and Nanotechnology (Biomedical Research Council, Agency for Science, Technology and Research, Singapore). M.R.R. would like to thank Karen Xuetong Liu for help with the initial screening of the reaction conditions.

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