



# Synthesis of 5- to 8-membered cyclic carbonates from diols and CO<sub>2</sub>: A one-step, atmospheric pressure and ambient temperature procedure



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## ABSTRACT

6-, 7- and 8-membered ring cyclic carbonates are of particular interest as monomers for ring-opening polymerisation towards more sustainable polymers. They are traditionally synthesised from diols and phosgene derivatives, and while alternative CO<sub>2</sub> methods exist to make 5- and 6-membered cyclic carbonates, there is no report of the synthesis of 7- and 8-membered cyclic carbonates made directly from CO<sub>2</sub>. Herein we report an efficient one-pot synthesis of cyclic carbonates which uses diols, CO<sub>2</sub>, tosyl chloride and mild bases (NEt<sub>3</sub> or TMP), under ambient temperature and 1 atm of CO<sub>2</sub> pressure. Fifteen cyclic carbonates were synthesised, including twelve known monomers, and the first examples of 7- and 8-membered cyclic carbonates made using CO<sub>2</sub>.

## 1. Introduction

The combination of depleting fossil fuel resources and the environmental persistence of traditional petroleum-derived polymers has been fuelling a wide research interest into sustainable polymers. Poly(carbonates) have been identified as promising such materials [1] as they can be obtained from natural feedstocks [2,3], and show biodegradability [4,5] and comparable thermal properties to crude-oil derived plastics [6–8]. Traditionally, the production of poly(carbonates) relies on the utilisation of phosgene and its derivatives, including dialkyl or diaryl carbonates, either by direct polycondensation with diols [9–12], or via the ring-opening polymerisation (ROP) of phosgene-derived, cyclic carbonate monomers (usually 6-, 7-, 8- or strained 5-membered rings) [13–15]. CO<sub>2</sub> has been investigated as a cheap, non-toxic, abundant, and renewable replacement for phosgene in these applications, primarily via its utilisation in the synthesis of dialkyl carbonates [16,17]. The direct coupling of CO<sub>2</sub> with epoxides (or oxetanes) to form cyclic [18,19] or polycarbonates [20,21] is now also a well-established reaction, however it suffers from several limitations, such as restricted access to substrates and monomer units limited to 5 or 6 atoms. Broadening the scope of CO<sub>2</sub> utilisation to polymer with longer linkages is worth pursuing as poly(carbonates) made by ring-opening polymerisation (ROP) of functionalised 8-membered cyclic carbonates have for example recently shown great potential, including in the biomedical field [14,22–24]. It would also allow to incorporate a wider

range of bio-based molecules into sustainable polycarbonates. However, there is currently no reported synthetic procedure to make such large rings from CO<sub>2</sub>.

The direct coupling of CO<sub>2</sub> with diols to form cyclic and poly(carbonates) has the potential to realise this goal as diols with potentially any structure and linkages length could be in theory be used. However, this ideal reaction is limited by kinetics and thermodynamics [25], and consequently, while several homogeneous and heterogeneous catalytic protocols have been developed [26–31], they require a large excess of chemical dehydrating agents to obtain high yields (e.g. propylene oxide [32], 2-cyanopyridine [26,27] or bromobutane [29]). Furthermore, very few of these procedures work under low CO<sub>2</sub> pressure, or have been applied to substrates other than 1,2-diols. It is indeed worth mentioning that 5-membered cyclic carbonates are usually not prone to ring-opening polymerisation (except when their ring-strain is large, as for products 8b and 9b, *vide infra*). Scheme 1 presents some of the methodologies reported for the direct coupling of CO<sub>2</sub> with 1,3-diols into 6-membered cyclic carbonates monomers. Recently, we developed a 2-step procedure that used strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and a tosyl chloride/triethylamine (NEt<sub>3</sub>) leaving/dehydrating group strategy, to form 6-membered cyclic carbonates at ambient temperature and low CO<sub>2</sub> pressure in chloroform (Scheme 1) [33]. This procedure has since been applied in the synthesis of chiral sugar-based cyclic carbonate monomers, the resulting polymers of which displayed interesting thermal properties, semi-crystallinity and

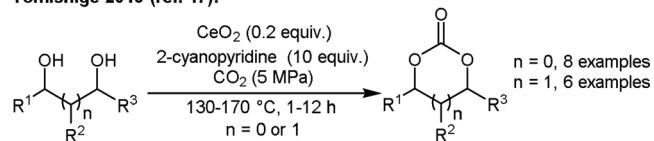
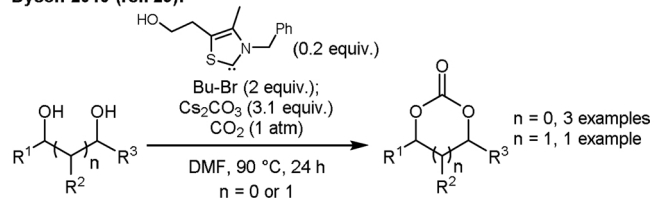
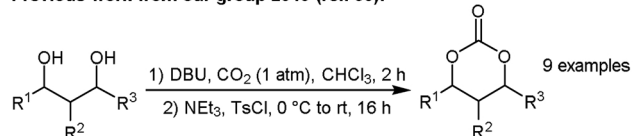
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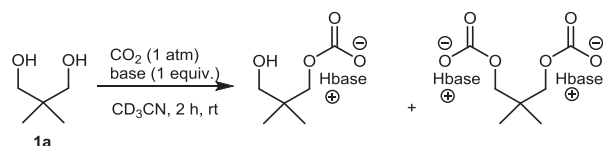
**Tomishige 2015 (ref. 17):****Dyson 2016 (ref. 29):****Previous work from our group 2015 (ref. 33):****Scheme 1.** Key papers on the direct coupling of CO<sub>2</sub> with diols into cyclic carbonates monomers (6-membered rings).

functionalisation potential [34–36]. However, this methodology has been hampered by the need for two sequential steps, as well as the use of a strong and moisture sensitive base (DBU).

Herein, we report a simplified one pot/one step procedure for the synthesis of cyclic carbonate from diols using only stoichiometric amounts of tosyl chloride and mild bases (all common reagents, and more benign than traditional phosgene derivatives such as triphosgene), under 1 atm. of CO<sub>2</sub> pressure and at ambient temperature. The protocol has been successfully applied to the synthesis of a wide scope of cyclic carbonates, including the first reported examples of 7- and 8-membered cyclic carbonates synthesised directly from CO<sub>2</sub> and three novel compounds.

**2. Results and discussion**

In a effort to increase the applicability of our previous approach, various commercially available mild bases were tested for CO<sub>2</sub> insertion with 2,2-dimethyl-1,3-propanediol, **1a** as the model substrate, and compared with DBU. In these tests, less toxic, non-chlorinated

**Table 1**  
CO<sub>2</sub> insertion into **1a** facilitated by pyridine, TMP, NEt<sub>3</sub> and DBU in CD<sub>3</sub>CN.<sup>[a]</sup>

Entry	Base	% Insertion	Monocarbonate	Biscarbonate
1	DBU	85%	59%	41%
2	TMP	2% <sup>[b]</sup>	100%	0%
3	NEt <sub>3</sub>	4%	100%	0%
4	Pyridine	0%	–	–

<sup>[a]</sup> **1a** (1.7 mol L<sup>-1</sup> in MeCN-D<sub>3</sub>), base (1 equiv.), CO<sub>2</sub> (1 atm), 2 h, room temperature (rt).

<sup>[b]</sup> NMR taken in CDCl<sub>3</sub> due to insolubility of 2,2,6,6-tetramethylpiperidinium salts in CD<sub>3</sub>CN.

**Table 2**One pot, two steps cyclocarbonation of **1a** with CO<sub>2</sub>.<sup>[a]</sup>

Entry	Base (1 <sup>st</sup> equiv.)	Base (2 <sup>nd</sup> equiv.)	Conversion to cyclic carbonate <b>1b</b> <sup>[b]</sup>
1	DBU	NEt <sub>3</sub>	78%
2	NEt <sub>3</sub>	NEt <sub>3</sub>	81%
3	TMP	TMP	89%

<sup>[a]</sup> One pot, two steps procedure: diol (1.7 mol L<sup>-1</sup> in MeCN), DBU (1 equiv.), CO<sub>2</sub> (1 atm), 2 h, then NEt<sub>3</sub> (1 equiv.), TsCl (1 equiv., 0.5 mol L<sup>-1</sup>), 0 °C to rt. Final diol concentration is then 0.4 mol L<sup>-1</sup>.

<sup>[b]</sup> Determined by relative integration in the <sup>1</sup>H spectrum (CDCl<sub>3</sub>) of product methylene signal (4.01 ppm, 4 H) vs aromatic signal in internal standard 1,3,5-trimethoxybenzene (6.01 ppm, 3 H).

acetonitrile could advantageously replace the chloroform previously used. Compared with DBU, 2,2,6,6-tetramethylpiperidine (TMP) and NEt<sub>3</sub> were found to only promote a small amount of CO<sub>2</sub> mono-insertion into the diol (Table 1 and Fig. S32), in agreement with pK<sub>a</sub> considerations (18.6 and 18.8 respectively vs 24.3 for DBU in acetonitrile) [37,38].

Nevertheless, the desired cyclic carbonate **1b** could be obtained more efficiently using NEt<sub>3</sub> and TMP than with the combination of DBU and NEt<sub>3</sub> (Table 2), including as previously reported in chloroform [33].

Furthermore, we pleasingly found that the reaction could be carried out in a single step, without the need for sequential addition of reagents, and that the cyclic carbonate product, **1b**, then formed in higher conversion than with our previous DBU-based, two step procedure (Table 3, entries 2 and 7 vs. entry 1). Conversion and selectivity of the reaction with both NEt<sub>3</sub> and TMP was however found to be highly dependent on the solvent, with maximum product formation and best selectivity observed in acetonitrile (Table 3, entries 2–4 and 7, 12–13).

Formation of **1b** also significantly decreased with increasing temperature (Table 3, entries 5–6 vs entry 2), alongside a higher proportion of tosylated side products (higher temperatures favouring deinsertion of

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