Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

A CATALYTIC DOMINO APPROACH TOWARD OXO-ALKYL CARBONATES AND POLYCARBONATES FROM CO_2, PROPARGYLIC ALCOHOLS, AND (MONO- AND DI-)ALCOHOLS

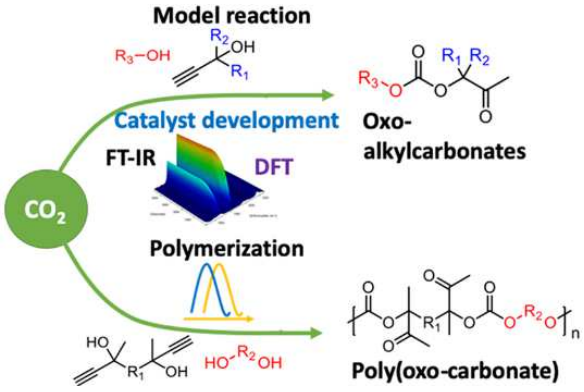
Charlene Ngassam Tounzoua[a], Bruno Grignard[a], Antoine Brege[a], Christine Jerome[a], Thierry Tassaing[b], Raphael Mereau[b], and Christophe Detrembleur[a]

[a] *Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium*

[b] *Institut des Sciences Moléculaires, UMR 5255 CNRS Université Bordeaux, 351, Cours de la Libération, F-33405 Talence, Cedex, France*

Keywords: CO_2 , Polycarbonates, Exovinylene cyclic carbonate, Catalysis, Mechanism

Abstract



We have explored the domino reaction between propargylic alcohols, carbon dioxide, and various alcohols with the double objective to prepare oxo-alkyl carbonates with a high yield and selectivity under mild conditions and to extend the process to the synthesis of phosgene-free polycarbonates. We first searched for a common catalytic system that was highly selective for the two reactions involved in the domino process, i.e., the cycloaddition of CO_2 to propargylic alcohol to yield α-alkylidene cyclic carbonate (αCC) and the alcoholysis of αCC to furnish oxo-alkyl carbonate. Kinetics studies monitored by operando IR spectroscopy and supported by ^{1}H NMR analyses and DFT modeling have permitted us to identify an efficient binary catalytic system composed of a combination of tetrabutylammonium phenolate [TBA][OPh] and silver iodide (AgI) (or copper iodide (CuI)) and to understand its action mode. The [TBA][OPh]/AgI catalytic system (5 mol %) was then successfully implemented for the selective preparation of a range of oxo-alkyl carbonates by the domino reaction with alcohols and propargylic alcohols of different structures. Most of these oxo-alkyl carbonates were produced at a high yield (≥97%) under mild operating conditions, i.e., at 60 °C and 1 bar of CO_2. The one-pot synthesis of various poly(β -oxo-carbonate)s from bis(propargylic alcohol)s, diols, and CO_2 was finally investigated, and the best operating conditions ([TBA][OPh]/AgI (10 mol %), 60 °C, 15 bar) afforded polycarbonate oligomers with weight-average molar masses of 4300 g/mol. Although the system should be optimized to produce longer polymer chains, this process offers a new phosgene-free alternative to the synthesis of functional polycarbonates poly(β-oxo-carbonate)s) under mild conditions.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

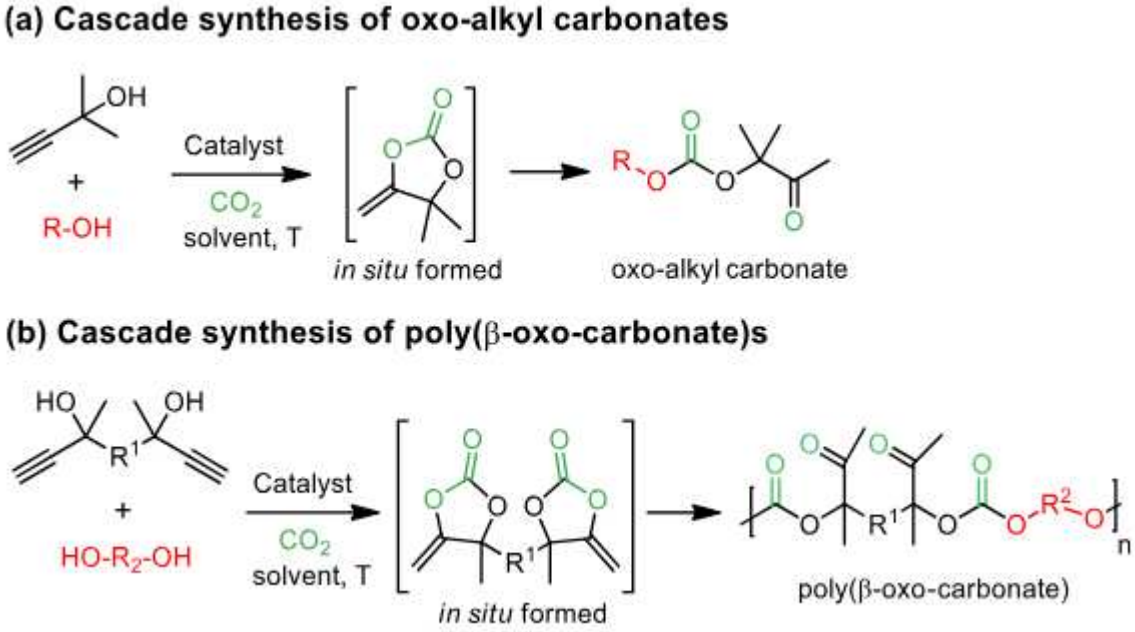
Introduction

Today, the upsurge in CO_2 utilization as renewable C1 feedstock has opened avenues in modern chemistry for the synthesis of a large diversity of (novel) organic scaffolds (e.g., organic carbonates, [1–5] carbamates, [6,7] oxazolidones, [5,8–11] carboxylic acids, [12–14] etc.) and polymers [15] (e.g., polycarbonates, [16–19] polyurethanes, [20–23] polyesters, [24] polyureas [25,26]). Among them, α-alkylidene 5-membered cyclic carbonates (αCCs) are emerging as a novel class of CO_2-sourced building blocks highlighted by BASF as promising molecules for organic and polymer chemistries. [27] They are typically synthesized by a 100% atom efficiency carboxylative coupling of CO_2 to propargylic alcohols, [28–32] with some of them that are easily accessible from acetylene and industrial formaldehyde waste. [33] Unlike the conventional 5-membered cyclic carbonates, α-alkylidene 5-membered cyclic carbonates display a remarkable reactivity toward amines, alcohols, and thiols to afford urethanes [34] (oxazolidones or β-oxo-carbamates [35,36]), β-oxo-alkyl carbonates, [37,38] and thiocarbonates or sulfur-containing tetrasubstituted ethylene carbonates, [39,40] respectively. The presence of the exocyclic olefin increases the ring strain of the molecule and ensures the selective ring opening by the nucleophiles with the formation of an enol intermediate which tautomerizes into a ketone, thus acting as the driving force for the reaction. The unique chemical features of αCCs were exploited by our group to pioneer a novel route to CO_2-sourced polycarbonates with unprecedented microstructures [39] that already showed relevance as solid electrolytes for Li-ion batteries. [41,42] In contrast to the conventional synthesis of CO_2-sourced polycarbonates by the direct ring-opening copolymerization of CO_2 with epoxides, [43–46] our approach focused on the polyaddition of bis(α-alkylidene cyclic carbonate)s (bis-αCCs) to diols in the presence of an organobase as catalyst to afford regioregular and defect-free poly(β-oxo-carbonate)s at room temperature. Earlier this year, Schaub engineered a novel synthetic protocol to provide bisαCCs and also demonstrated their utility for the fabrication of low molar mass poly(β-oxo-carbonate)s ($M_n \sim$ 2000 g/mol). [47] However, the synthetic routes to bisαCCs are still tedious with demanding purification procedures. To curtail these boundaries, we introduce in this work a novel domino terpolymerization approach to produce poly(β-oxo-carbonate)s from a mixture of CO_2, bispropargylic alcohol, and diols (Scheme 1b), some of them being selected for their ease of production from lignin biomass. If many publications focused on the one-pot domino synthesis of oxazolidinones and oxopropyl carbamates from CO_2, propargylic alcohols and amines, [48–53] only few examples reported the preparation of oxo-alkyl carbonates by reacting propargylic alcohols, CO_2, and alcohols (Scheme 1a). The challenge lies in the identification of suitable catalysts capable of fixing CO_2 to propargylic alcohols to form αCCs *in situ* in a selective manner and to promote their alcoholysis. Song et al. reported on the synthesis of oxo-alkyl carbonates with yields of 22%–76% using DBU/Zn salts (40:20 mol %) as catalytic systems at 80 °C and 10 bar in 16 h. [54] Hu et al. obtained yields up to 99% with AgCl/butylmethylimidazolium acetate ([BMIm][OAc]) binary catalytic systems. However, the ionic liquid was added in large amounts (100 mol %) to promote the reaction at room temperature and atmospheric CO_2 pressure. 38 He's group used a combination of Ag_2CO_3 and PPh_3 to catalyze the formation of oxo-alkyl carbonate scaffolds with yields of 62%–78%. Working with a 0.5 equiv excess in the alcohol was required to obtain higher yields (98%). [55] Zhang reported high yields of 81%–93% and a large product scope using a silver sulfadiazine/EtNBr (5 mol %) dual system at 1 bar and 80 °C for 24 h. [56,57] This later system suffers from the multistep synthesis of sulfadiazine that is not a straightforward procedure. Although different

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

catalytic systems exist to provide simple αCCs and oxo-alkyl carbonates, none of them has been utilized for both the quantitative synthesis of bisαCCs and their *in situ* transformation into poly(β-oxo-carbonate)s in a cascade reaction. In addition, as previously exemplified, none of them supported the features needed to respond to the requirements of a step-growth polymerization process that is extremely sensitive to the stoichiometry of the reaction. The bisαCCs intermediate produced *in situ* by carboxylative cycloaddition of CO_2 to bis(propargylic alcohol) will be directly involved in the polyaddition to the diol. Any side reactions will therefore result in a deviation from the perfect stoichiometry and cause the termination of the domino terpolymerization. To pursue our goal, it is therefore crucial to identify operating conditions and a catalytic system compatible for both steps, i.e., the selective formation of bisαCC and its copolymerization with the diol.

Scheme 1. One-Pot Domino Synthesis of (a) Oxo-Alkyl Carbonates and (b) Poly(β-oxo-carbonate)s



In this work, we have developed a novel binary catalyst and evaluated its activity and selectivity on model compounds. Kinetic insights via operando FT-IR spectroscopy, correlated to mechanistic DFT calculations, enabled us to understand and rationalize the mode of action of the catalyst. We then used it to selectively synthesize oxo-alkyl carbonates of different structures by the domino reaction between CO_2, propargylic alcohols, and monoalcohols. Finally, this process was exploited for the preparation of PCs under mild operating conditions.

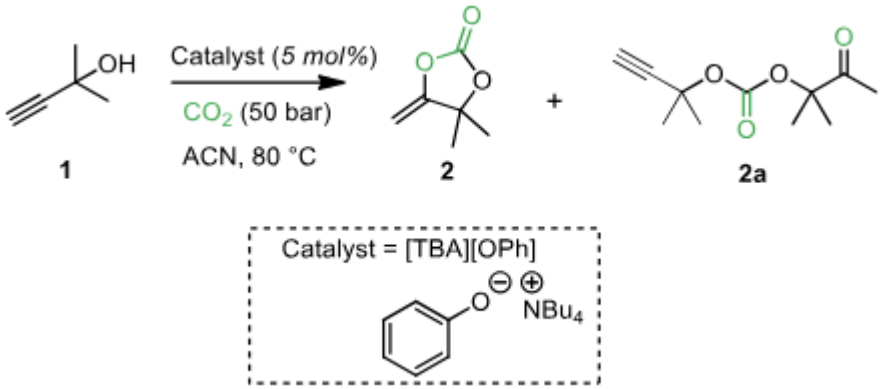
Results and Discussion

Catalyst Design and Optimization of Reaction Parameters. Model carboxylative coupling reactions of CO_2 with 2-methyl-3-butyn-2-ol to provide αCC were first screened (Scheme 2). We selected tetrabutylammonium phenolate ([TBA][OPh]) as the organocatalyst as we previously demonstrated its high efficiency for the envisioned reaction under moderate conditions. [58] This activity resulted from a good compromise between ion-pair separation controlled by steric effect and the basicity of the anion

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

as evidenced in a previous benchmarking study. [58] Moreover, it is easily prepared from cheap phenol, a biobased product derived from the fractionation of lignin. [59]

Scheme 2. Coupling of CO_2 to 2-Methyl-3-butyn-2-ol



The model reaction was carried out at 50 bar and 80 °C in acetonitrile with a low catalyst loading (5 mol %). Under these conditions, the expected αCCs **2** was produced with 90% yield in only 1 h (Table 1, entry 1). However, the main side reaction observed was the formation of the linear oxo-carbonate **2a** by the addition of the propargylic alcohol to αCCs. To extend the use of this catalytic system for the targeted domino reaction and prevent this side reaction, an optimization of both the reaction conditions and the catalyst structure was required.

Table 1. Influence of Temperature on Carboxylative Cyclization of CO_2 with 2-Methyl-3-butyn-2-ol Catalyzed by [TBA][OPh][a]

Entry	Temp. (°C)	Reaction time (h)	Conv. of 1 (%)	Selectivity for 2 (%)
1	80	1	100	90
2	60	1	20	99
3	60	6	100	96
4	40	1	6	99
5	40	24	100	99

[a]Conditions: 2-methyl-3-butyn-2-ol (2 mL, 0.02061 mol), [TBA][OPh] (5 mol %), acetonitrile (2 mL), CO_2(50 bar). The conversions and selectivities were determined by ^{1}H NMR spectroscopy in $CDCl_3$.

By decreasing the temperature to 60 °C, the reaction slowed down (6 h was required for full conversion), meanwhile the selectivity in **2** increased to 96%, with 4% of hydroxyketone formed from the hydrolysis of αCC (Table 1, entry 3). When we further decreased the temperature to 40 °C, the reaction rate decreased considerably with a propargylic alcohol conversion of only 6% after 1 h (Table 1, entry 4). Importantly, 2-methyl-3-butyn-2-ol was fully and selectively converted into the desired product **2** with no side product when the reaction time was extended to 24 h (Table 1, entry 5).

To improve the selectivity in αCC **2** without excessively compromising the reaction rate, we considered the use of a cocatalyst that was expected to activate the alkyne for the carboxylative addition. Some metal-based catalysts (such as monovalent silver and copper salts) are capable of pi-coordination with the alkyne bond and are therefore expected to be beneficial for this reaction. (60,61) Various salts were tested, and results are summarized in Table 2. Adding silver(I) or copper(I) salts favored the reaction. The best catalytic activity was obtained when [TBA][OPh] was combined with CuI or AgI, with

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

an increase in the conversion of **1** from 6% (without cocatalyst, Table 2, entry 1) to 81% (with CuI, Table 2, entry 7) or 100% (with AgI, Table 2, entry 3) in 1 h at 15 bar and 40 °C. Both [TBA][OPh]/CuI and [TBA][OPh]/AgI binary systems drove the reaction with a 100% selectivity in the targeted product **2** as confirmed by ^{1}H NMR spectroscopy (Figure S2). The difference in activity for the reactions carried out in the presence of the different silver salts (Ag_2CO_3, AgOAc, and AgI) is at this stage difficult to rationalize. However, the different solubility of the silver salts in the reaction medium might be at the origin of this observation. Indeed, when preparing the reaction medium before pressurization with CO_2, none of these cocatalysts were fully soluble. However, quantifying their solubility in the reaction medium under pressure was not possible.

Table 2. Screening of Cocatalyst and Solvents for Coupling of CO_2 to 2-Methyl-3-butyn-2-ol Catalyzed by [TBA][OPh][a]

Entry	Cocatalyst	Solvent	Conv. of 1 (%)	Selectivity for 2 (%)
1	–	ACN	6	100
2	Ag_2CO_3	ACN	70	100
3	AgI	ACN	100	100
4	AgOAc	ACN	38	100
5	CuCl	ACN	50	100
6	CuBr	ACN	47	100
7	CuI	ACN	81	100
8	CuI	$CDCl_3$	63	100
9	CuI	THF	70	100
10	CuI	DMSO	58	100
11	CuI	Neat	92	98

[a]Conditions: 2-methyl-3-butyn-2-ol (2 mL, 0.0206 mol), [TBA][OPh] (5 mol %), cocatalyst (5 mol %), solvent (2 mL), CO_2 (15 bar), 1 h, 40 °C. The conversions and selectivity were determined by ^{1}H NMR in $CDCl_3$ (see Figure S1 for the procedure).

We then screened some solvents using CuI as cocatalyst and found the reaction to be fastest in acetonitrile and slowest in DMSO (Table 2, entries 7 and 11), with the same selectivity in product **2** (100%).

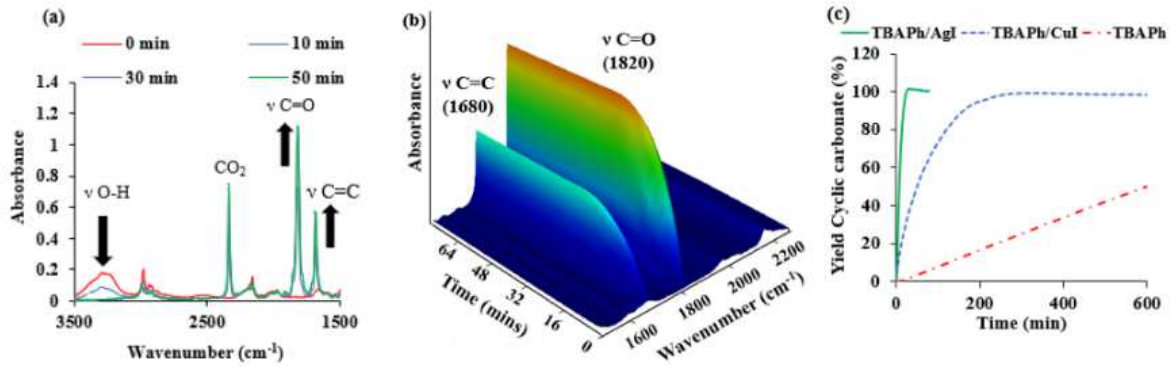
In prelude of our subsequent study on the preparation of poly(β-oxo-carbonate)s by the domino reaction, we selected DMSO as the solvent to continue our study. Unlike acetonitrile, its choice was justified by its capability to totally solubilize the bis-propargylic alcohol and provide homogeneous conditions at the initial stage of the reaction.

To benchmark the activity of the [TBA][OPh], CuI/[TBA][OPh], and AgI/[TBA][OPh] catalysts, we studied the kinetics of the reaction using online high pressure FT-IR spectroscopy at 40 °C using both CuI and AgI. Figure 1a shows an overlay of the IR spectra at different times obtained with the [TBA][OPh]/AgI system. We observed a signal at 3300 cm^{-1} corresponding to the OH band of the alkynol which decreased gradually overtime and the concomitant formation of the cyclic carbonate and exovinylene group with characteristic vibrations of ν C═O at 1823 cm^{-1} and ν C═C at 1680 cm^{-1}. The CO_2 band at 2330 cm^{-1} was observed and remained constant due to the large excess of CO_2 under the investigated conditions. A similar profile was obtained with the [TBA][OPh]/CuI system (Figure S3). By following the evolution of the ν C═O band at 1823 cm^{-1} (Figure 1b) over time, the yield in exovinylene cyclic

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

carbonate **2** was calculated for the reactions catalyzed by [TBA][OPh], [TBA][OPh]/CuI, or [TBA][OPh]/AgI systems (Figure 1c, see Supporting Information for the quantification procedure).

Figure 1. Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one by organocatalyzed coupling of CO_2 to 2-methyl-3-butyn-2-ol. (a) FT-IR spectra at different times for the [TBA][OPh]/AgI catalyzed reaction. (b) 3D profile of the 1500–2200 cm^{-1} region obtained by online FT-IR spectroscopy for the [TBA][OPh]/AgI catalyzed reaction. (c) Yield of cyclic carbonate for the different catalytic systems. Conditions: 2-methyl-3-butyn-2-ol (16 mL, 0.165 mmol), [TBA][OPh] (5 mol %), AgI or CuI (5 mol %), T = 40 °C, p_{CO2} = 15 bar, solvent = DMSO (V = 16 mL).

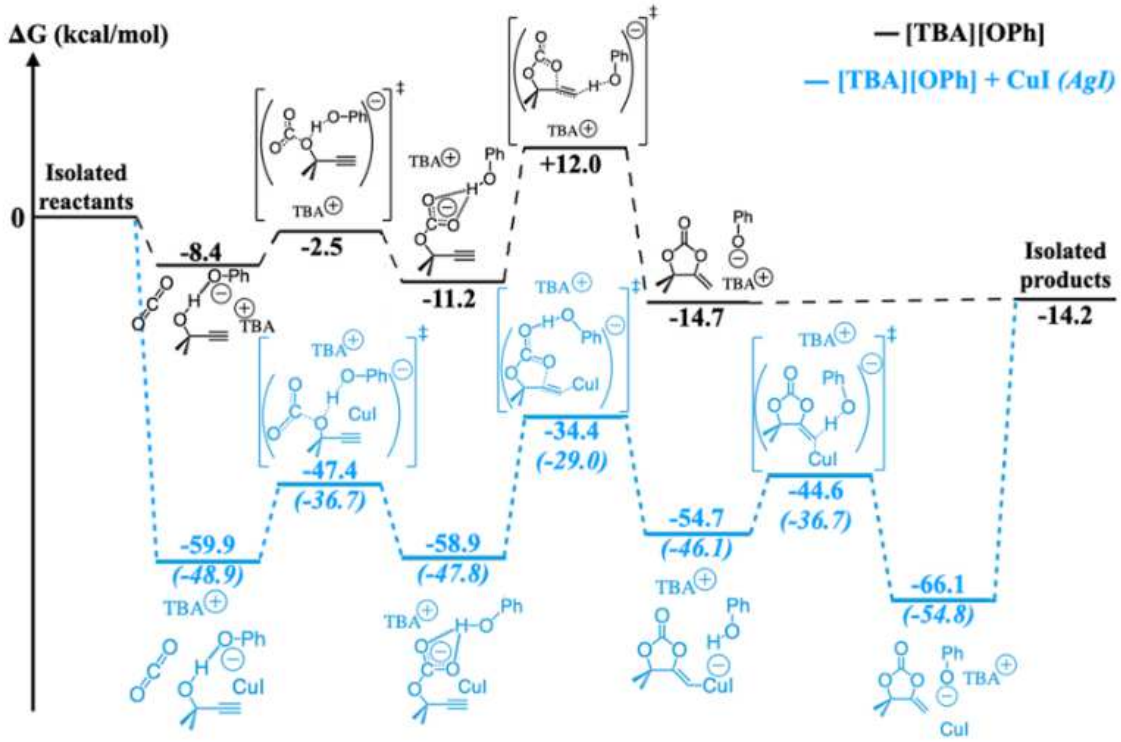


The cycloaddition was complete in 180 min with the [TBA][OPh]/CuI binary system, and in less than 50 min with the [TBA][OPh]/AgI system, no secondary product was detected as already noted during the batch screening tests. By using [TBA][OPh] as the sole catalyst, the reaction was extremely slow, requiring 24 h for completion, but remained selective. This comparative study highlights the synergistic role of the cocatalyst. It must be mentioned that few articles have been published with copper iodide as the cocatalyst for this reaction. Although high yields were obtained (70%–98%), moderate to high temperatures (60–120 °C) were most often required. [32] Room temperature operation was recently reported by using CuI in combination with phosphonium levulinate. However, a high pressure of CO_2 (p_{CO2} = 100 bar) was required, and the phosphonium salt was used in large amount (66 mol %). [60] Our system involving [TBA][OPh]/CuI is thus competitive for operating under mild reaction conditions, at a low catalyst loading (5 mol %).

The mechanism of the carboxylative cyclization of **1** was then investigated by DFT calculations (Figure 2) with the help of the M062X functional (see SI for details) where the Gibbs free energy of each structure is relative to the sum of the individual Gibbs free energies of the reactants for each pathway, i.e., propargylic alcohol + CO_2 + [TBA][OPh] for the reaction catalyzed by the sole [TBA][OPh] and propargylic alcohol + CO_2 + [TBA][OPh] + CuI (AgI) for the reaction catalyzed by [TBA][OPh]/CuI (AgI). For the sake of comparisons between the different systems, the starting point energies for all systems coincide with zero energy.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

Figure 2. Gibbs free energy profiles for α-methylene carbonate formation with [TBA][OPh], [TBA][OPh]/CuI, and [TBA][OPh]/AgI as catalytic systems.



We initially explored the reaction pathway with [TBA][OPh] as catalyst only, which is composed of two elementary steps. From the van der Waals complex that exhibits hydrogen bonding between the oxygen atom of the phenolate anion and the hydrogen atom of the hydroxyl group of 2-methyl-3-butyn-2-ol, the first step consists of the deprotonation of the propargylic alcohol simultaneously to the nucleophilic attack onto the carbon atom of CO_2 with the formation of a carbonate anion intermediate (−11.2 kcal·mol^{-1}). The activation barrier of this first step is calculated to be 5.9 kcal·mol^{-1}, and as the transition state associated with it is submerged with respect to the separated reactant limit (fixed at the zero Gibbs free energy), it is supposed to occur very quickly. The second step, which is the rate-determining step with a barrier height of 23.2 kcal·mol^{-1}, involves the intramolecular nucleophilic addition from the carbonate anion to the C≡C bond and the simultaneous protonation of the alkenyl anion by the PhOH leading to the formation of **2** and the regeneration of the [TBA][OPh] catalyst.

In the presence of CuI or AgI as the cocatalyst, the Gibbs free energy profile encountered an important exothermicity (about tens of kcal·mol^{-1}), which considerably accelerated the reaction kinetics as observed experimentally. While the first step of the whole reaction is identical to the one with the sole [TBA][OPh] catalyst, the two remaining steps to form target product **2** are thus as follows: (i) The ring formation occurrs from the carbonate anion together with the attack of CuI (AgI) on the C≡C bond with an associated Gibbs free energy barrier of 24.5 kcal·mol^{-1} (18.8 kcal·mol^{-1}). (ii) From the alkenyl metal intermediate a proto-demetalation takes place, and the final product is formed by hydrogen proton transfer from PhOH. The Gibbs free energy activation barrier of this last step is calculated to be 10.1 and 9.4 kcal·mol^{-1} for the cocatalysis with CuI and AgI, respectively.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

To summarize, after the first step of the overall process (addition of CO_2 to the propargylic alcohol), the reactants have to overcome the highest energy transition state of +12 kcal·mol^{-1} for the reaction catalyzed by [TBA][OPh] only. In contrast, due to the strong exergonicity observed in the presence of CuI (AgI), the reactants might spontaneously react without any stabilization and accelerate the reaction kinetic compared to the case of the reaction catalyzed by [TBA][OPh] only. On the other hand, in the presence of CuI (AgI), the remaining part of the species that could be stabilized must undergo activation energies of 18.8 and 23.2 kcal·mol^{-1} for the reactions cocatalyzed by AgI and CuI, respectively, indicating that the reaction catalyzed by [TBA][OPh]/AgI is the fastest which is in good agreement with the kinetics studies by online FT-IR experiments. As the binary [TBA][OPh]/AgI systems displayed the highest catalytic activity, it was selected to pursue our objectives of domino reactions and polymerizations.

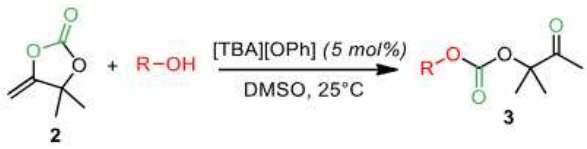
Synthesis of Oxo-Alkyl Carbonates. We then evaluated the capacity of the [TBA][OPh] and [TBA][OPh]/AgI dual systems to catalyze the alcoholysis of αCC **2** into oxo-alkyl carbonates **3** at room temperature (T = 25 °C) in DMSO. The reaction was tested for different alcohols, and the results are summarized in Table 3. Importantly, [TBA][OPh] (5 mol %) displayed sufficient basicity to enable the complete and selective conversion of αCC **2** into the corresponding oxo-alkyl carbonate **3** when reacted with 1-butanol for 1 h at 25 °C, while no reaction was noted without the catalyst (Table 3, entries 1 and 2). The [TBA][OPh] acted as a hydrogen bond acceptor, thereby activating the alcohol molecule. When AgI was used as the cocatalyst in combination with [TBA][OPh], αCC **2** was selectively converted into oxo-alkyl carbonate (Table 3, entry 3), similarly to the reaction performed with [TBA][OPh] only (Table 3, entry 2). The addition of AgI did not induce any side reaction, at least during the investigated reaction period. We repeated this experiment for a shorter reaction time (15 min instead of 1 h), and an identical conversion of **2** (100%) and selectivity for **3** (100%) were again noted. Although further experiments would be required, it suggests that silver salt has no noticeable effect on the alcoholysis of the α-alkylidene cyclic carbonate, in line with reports of Li et al. [56] and Han et al. [38]

When using benzyl alcohol, the reaction carried out with [TBA][OPh] was also fast, quantitative, and selective (Table 3, entry 4). In addition, the selectivity was still excellent, and the conversion in αCC dropped to 68% when using a less reactive secondary alcohol, 2-propanol, under identical conditions (Table 3, entry 5). No reaction was however noted with the tertiary alcohol, 2-methyl-2-butanol (Table 3, entry 6). The lower reactivities of the secondary and tertiary alcohols arose from their steric hindrance that decreased their nucleophilic character.

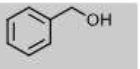
Cascade Reaction on Model Compounds. As [TBA][OPh]/AgI was able to catalyze both the selective formation of DMACC by coupling CO_2 to 2-methyl-3-butyn-2-ol and its alcoholysis by primary and secondary alcohols, we then evaluated its capacity to catalyze the one-pot cascade synthesis of the corresponding oxo-alkyl carbonate **3** from CO_2, 2-methyl-3-butynol, and 1-butanol (Table 4). The reactions were carried out at 15 bar for 6 h, using 5 mol % of [TBA][OPh] with and without AgI, and different temperatures were screened. Results are presented in Table 4.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

Table 3. Alcoholysis of 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (αCC, **2**) Catalyzed by [TBA][OPh][a]

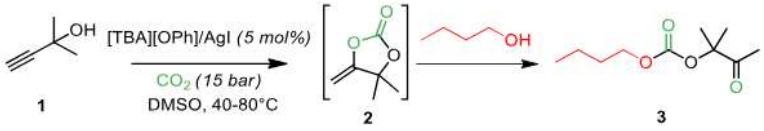


2 3

Entry	Catalyst	Alcohol	Alcohol structure	Conv. of 2 (%)	Yield in 3 (%)
1	-	1-butanol	C_4H_9OH	0	0
2	[TBA][OPh]	1-butanol	C_4H_9OH	100	100
3	[TBA][OPh]/AgI	1-butanol	C_4H_9OH	100	100
4	[TBA][OPh]	benzyl alcohol		100	100
5	[TBA][OPh]	propan-2-ol		68	100
6	[TBA][OPh]	2-methyl-2-butanol		0	/

[a]Conditions: αCC**2** (0.5 g, 3.904 mmol), alcohol (3.904 mmol), [TBA][OPh] (66 mg, 5 mol %), cocatalyst (AgI or CuI: 5 mol %), DMSO (1 mL), T = 25 °C, t = 1 h. The conversions and selectivities were determined by ^{1}H NMR in DMSO-d_6. (see Figure S4 for the procedure).

Table 4. Cascade Synthesis of Butyl-(2-methyl-3-oxobutan-2-yl) Carbonate from 2-Methyl-3-butyn-2-ol, CO_2, and Primary Alcohol 1-Butanol[a]



1 2 3

Entry	Catalyst	T (°C)	Conv. of 1 (%)	2[b](%)	3[c] (%)
1	[TBA][OPh]	40	0	0	0
2	[TBA][OPh]	60	0	0	0
3	[TBA][OPh]	80	15	100	0
4	[TBA][OPh]/AgI	40	100	93	7
5	[TBA][OPh]/AgI	60	100	80	20
6	[TBA][OPh]/AgI	80	100	23	74

[a]Conditions: 2-methyl-3-butyn-2-ol (2 mL, 0.02061 mol), 1-butanol (1.89 mL, 0.02065 mol), [TBA][OPh] (5 mol %), AgI (5 mol %), DMSO (2 mL), CO_2 (15 bar), 6 h.[b]Selectivity for **2**.[c]Selectivity for **3**. The conversions and selectivity were determined by ^{1}H NMR in DMSO-d_6. (see Figure S5 for the procedure).

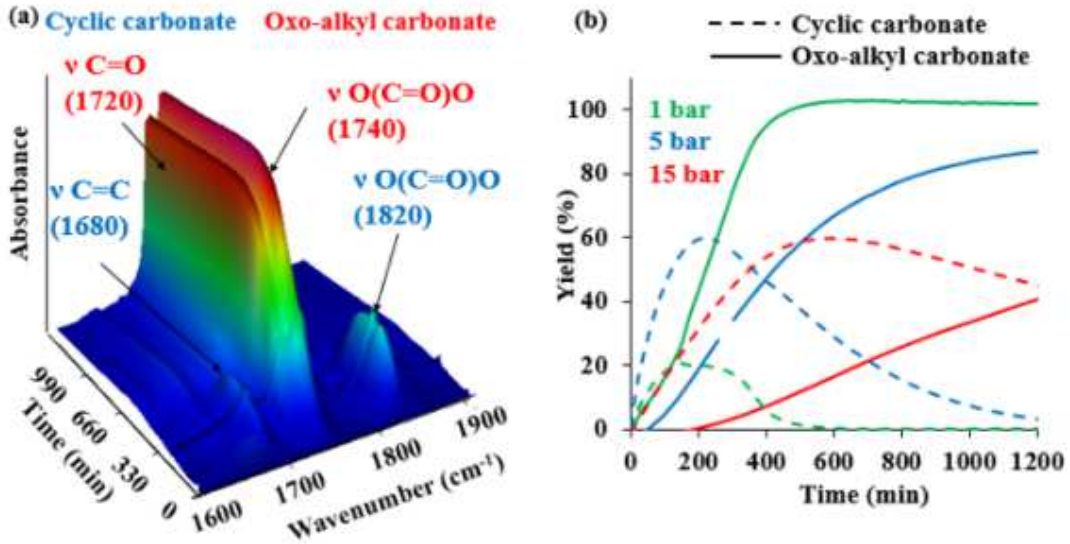
While there is little to no reaction in the absence of AgI (Table 4, entries 1–3), full conversion of **1** was achieved at 40 °C after 6 h of reaction for the [TBA][OPh]/AgI system (Table 4, entry 4). However, the main product was αCC **2** (93%), with only 7% of the desired oxo-alkyl carbonate **3**. By raising the reaction temperature to 60 or 80 °C, the yield in **3** was increased to 20% or 74%, respectively (Table 4, entries 5 and 6).

The influence of the working pressure on the yield and selectivity of the reaction was then evaluated by online IR spectroscopy at 60 °C. Unfortunately, because the bands corresponding to the CC triple bond (890 and 960 cm^{-1}) and the OH bond (3260 cm^{-1}) of the propargylic alcohol overlapped with other bands, we could not follow the consumption of the propargylic alcohol over time. However, by analyzing a sample of the reaction mixture at the end of each experiment by ^{1}H NMR spectroscopy, we could confirm the total conversion of the propargylic alcohol for reactions performed at p_{CO2} of 1, 5, or

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

15 bar. We monitored the formation of αCC **2** and its conversion into the oxo-alkyl carbonate **3** by following the evolution of the carbonyl band of the cyclic carbonate **2** at 1820 cm^{-1} and of the linear carbonate **3** at 1740 cm^{-1} (Figure 3a). The yields of each product are plotted vs time in Figure 3b. At 60 °C and 15 bar of CO_2, the formation of the oxo-alkyl carbonate **3** was observed after about 2.5 h of reaction and was relatively slow. After 20 h of reaction, a mixture of product **2** (45%) and **3** (40%) was collected. By decreasing the CO_2 pressure to 5 bar, the formation of αCC **2** was faster, and its conversion into **3** started after 45 min. After 20 h, the yield in **2** was only 3%, while the desired product **3** was formed with 87% yield. Importantly, when the pressure was further reduced to 1 bar, αCC **2** was rapidly formed and was simultaneously converted into **3**. The domino reaction was complete in less than 10 h at 1 bar and selective toward the formation of **3**. These kinetics studies clearly highlight that a low CO_2 pressure was required for an efficient domino reaction and for the selective production of **3**. It was assumed that high CO_2 pressure favored the carbonation of 1-butanol, consequently deactivating it for the alcoholysis of the αCC **2** formed *in situ*.

Figure 3. One-pot domino synthesis of butyl-(2-methyl-3-oxobutan-2-yl) carbonate from CO_2, 2-methyl-3-butyn-2-ol, and 1-butanol catalyzed by [TBA][OPh]/AgI at 60 °C. (a) 3D profile for a reaction conducted at p_{CO2} of 1 bar and (b) influence of CO_2 pressure on the formation of cyclic carbonate **2** and oxo-alkyl carbonate **3**. Conditions: [TBA][OPh] (5 mol %), AgI (5 mol %), 2-methyl-3-butyn-2-ol (12 mL), 1-butanol (11.3 mL), DMSO (12 mL).

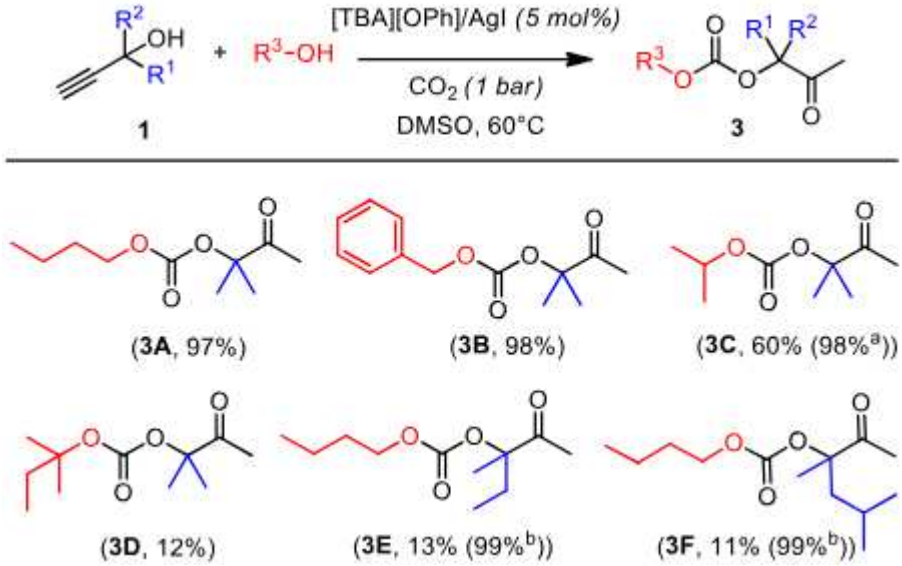


To give an additional clue to this hypothesis, we monitored by online FT-IR spectroscopy the possible formation of a zwitterionic compound from 1-butanol, CO_2, and [TBA][OPh] in the solvent used for the reaction (DMSO) at a pressure of 15 bar. We indeed observed the rapid growth (<5 min) of a band at 1660 cm^{-1} which is typical of the ν C═O of a carbonate anion, [62] thus supporting the *in situ* carbonation of 1-butanol favored at high pressure of 15 bar (Figure S6).

To highlight the versatility of the [TBA][OPh]/AgI catalytic system for the domino reaction under the optimum conditions (60 °C, p_{CO2} = 1 bar, 10 h), we enlarged the scope of propargylic alcohols and monoalcohols to access various oxo-alkyl carbonate compounds (Scheme 3).

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

Scheme 3. Product Scope for Synthesis of Oxo-Alkyl Carbonates*



*Conditions: propargylic alcohol (20.61 mmol), aliphatic alcohol (20.61 mmol), [TBA][OPh]/AgI (5 mol %), DMSO (2 mL), p_{CO2} = 1 bar, t = 10 h. Yields were determined by ^{1}H NMR spectroscopy in DMSO-d_6 after 24 h[a] and 72 h[b]. ^{1}H and ^{13}C NMR as well as FT-IR characterizations are illustrated in Figures S7–S21.

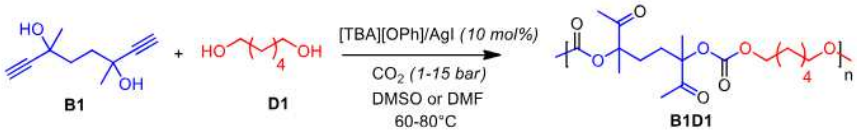
In all cases, all propargylic alcohols were fully consumed. The corresponding oxo-alkyl carbonates were formed with a high yield (≥97%) when primary alcohols such as 1-butanol or benzyl alcohol were involved with the less sterically hindered propargylic alcohol, 2-methyl-3-butyn-2-ol. When a secondary alcohol 2-propanol or tertiary alcohol 2-methyl-2-butanol was employed together with 2-methyl-3-butyn-2-ol, the yields in oxo-alkyl carbonate dropped to 60% (product **3C**) and 12% (product **3D**), respectively. Similarly, when 1-butanol was reacted with more sterically hindered propargylic alcohols such as 3-methyl-1-pentyn-3-ol and 3,5-dimethyl-1-hexyn-3-ol; very low yields (13% for product **3E** and 11% for product **3F**), respectively, were obtained. The remaining percentage corresponded to the unreacted cyclic carbonate intermediate. Interestingly, by extending the reaction time to 72 h, the selectivity and yield in the target oxo-alkyl carbonates increased to 99% for both **3E** and **3F**.

Synthesis of Poly(*β*-oxo-carbonate)s by One-Pot Domino Terpolymerization. The reaction conditions were first optimized for the terpolymerization of 4,4'-(ethane-1,2-diyl)bis(4-methyl-5-methylene-1,3-dioxolan-2-one) **B1**, 1,6-hexanediol **D1**, and CO_2 using [TBA][OPh]/AgI as the binary catalytic system (Table 5). When carried out in DMSO at 1 bar of CO_2, oligomers with a number average molar mass (M_n) of 1000 g/mol were collected after 48 h at 60 °C (Table 5, entry 1). By increasing the CO_2 pressure to 15 bar, M_n was increased to 1500 g/mol; however, no significant evolution was observed when the reaction time was extended to 72 h (Table 5, entries 2 and 3). When the reaction was performed under neat conditions, similar results were obtained. Interestingly, the molar mass was almost doubled when using DMF as solvent (Table 5, entries 8–9). Increasing the reaction temperature to 80 °C was detrimental to the polymerization with the formation of oligomers of lower M_n (Table 5, entries 4 and 5 in DMSO and entry 10 in DMF). Several factors might be at the origin of this observation. First, we demonstrated that increasing the reaction temperature decreased the selectivity in the *in situ* formed

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

α-alkylidene cyclic carbonate (Table 1), with the consequence that the stoichiometry between the α-alkylidene cyclic carbonate and alcohol groups is not respected. Second, some thermally induced side reactions (e.g., transcarbonation) might consume reactive groups and thus will provoke a deviation from the perfect stoichiometry, thus lowering the polymer molar mass. This second hypothesis is currently under investigation.

Table 5. Screening of Parameters for One-Pot Domino Synthesis of Poly(β-oxo-carbonate)s

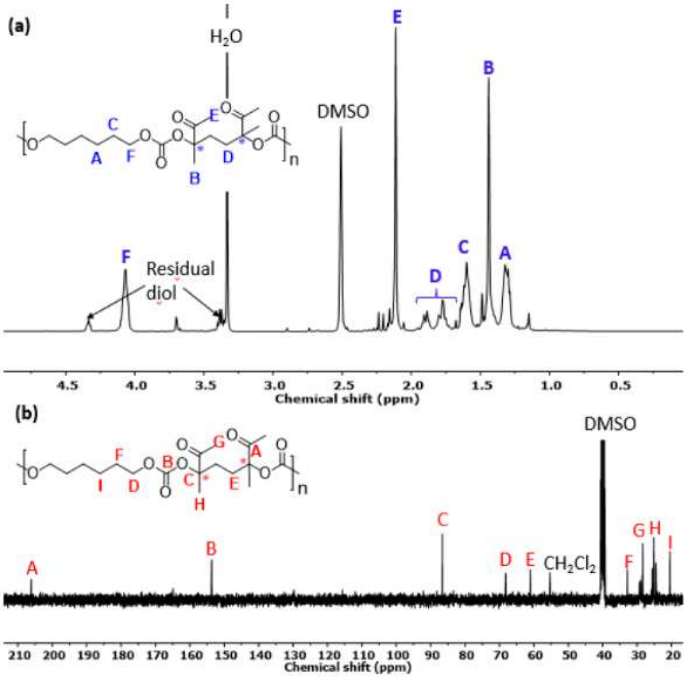


Entry	Solvent	*P* (bar)	*T* (°C)	Time (h)	Conv. of B_1[b] (%)	Conv. of D1[c] (%)	M_n[c] (g/mol)	M_w[c] (g/mol)	PDI[c]
1	DMSO	1	60	48	100	20	<1000	–	–
2	DMSO	15	60	24	100	61	1500	1900	1.3
3	DMSO	15	60	72	100	55	1700	2300	1.3
4	DMSO	15	80	24	100	44	1500	1900	1.3
5	DMSO	15	80	72	100	50	1500	1800	1.2
6	Neat	15	60	24	100	35	1400	1700	1.2
7	Neat	15	60	72	100	62	2150	3100	1.4
8	DMF	15	60	24	100	73	2700	4300	1.6
9	DMF	15	60	72	100	65	2600	3900	1.5
10	DMF	15	80	72	100	60	1600	1950	1.2

[a]Conditions: bis(propargylic alcohol) **B1** (0.3 g, 1.802 mmol), 1,6 -hexanediol (**D1**) (0.213 g, 1.802 mmol), [TBA][OPh]/AgI (10 mol %), [bis(propargylic alcohol)] = 1.8 M when a solvent was used.[b]Determined by ^{1}H NMR spectroscopy.[c]Determined on crude products by GPC using DMF as eluent with PS standard.

The SEC elugrams obtained on the crude reaction media (in order to avoid any fractionation of the sample during purification) are presented in Figures S23–25. They show that polymers prepared in DMF were of higher molar mass compared to those produced in DMSO or in the bulk. In the two latter cases, dimers and trimers, were clearly observed. Dispersities were rather low for a step-growth polymerization process but are the result of the low molar mass polymers.

Figure 4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra in DMSO-d_6 of purified poly(β-oxo-carbonate) **B1D1**.

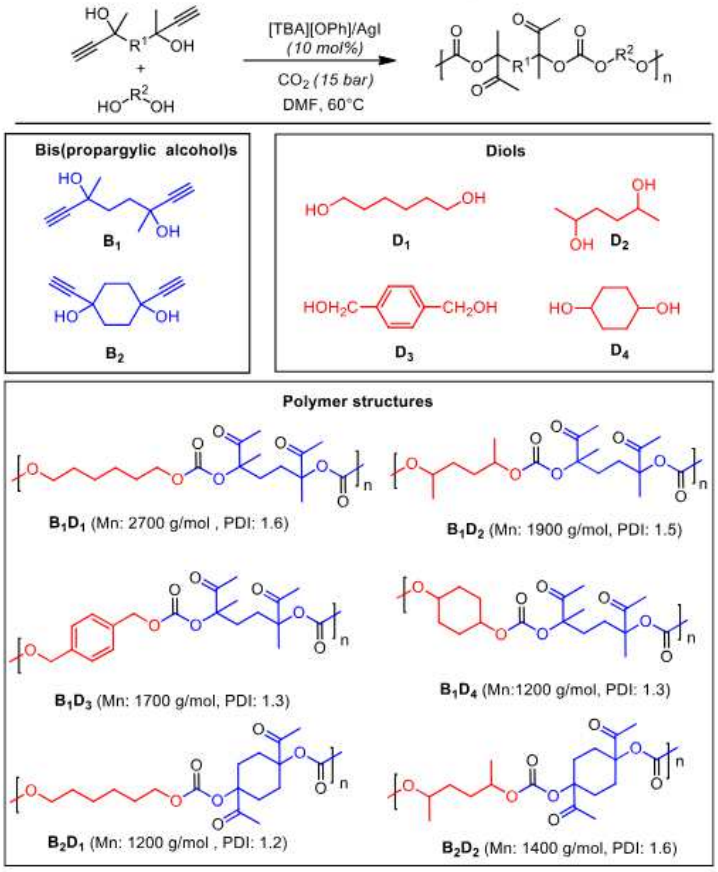


Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

The structure of the poly(β-oxo-carbonate) was evidenced by ^{1}H NMR spectroscopy (Figure 4a) by the presence of singlets at δ = 2.11 ppm typical of the methyl group in the α position of the ketone, at δ = 1.44 ppm, characteristic of the methyl group in alpha of the carbonate, and at δ = 4.06 ppm, characteristic of the methylene linked to the carbonate group. The ^{13}C NMR (Figure 4b) analysis of the polymer evidenced the resonance of the ketone at δ = 206 ppm and the carbonate at δ = 153 ppm. All assignments were confirmed by COSY, HSQC, and HMBC analyses (Figures S28–30).

The substrate scope was extended by testing other diols (primary **D3** and secondary **D2** and **D4**) and a cycloaliphatic bis(propargylic alcohol) (**B2**) (Scheme 4). The corresponding poly(β-oxo-carbonate)s were obtained in all cases, with the structures that were confirmed by ^{1}H NMR analyses (Figures S31–S35). Although the molar masses of the polymers cannot be compared (they are obtained based on a polystyrene calibration and the polymers are characterized by different hydrodynamic volumes), the highest M_n of 2700 g/mol (M_w = 4300 g/mol) was obtained for **B1D1** (Scheme 4). Lower molar masses were collected for polymers prepared from the cycloaliphatic bis(propargylic alcohol) **B2**. As both **B2D1** and **B2D2** copolymers were only partly soluble in DMF at room temperature, and because no common organic solvent could totally dissolve them, fractionation of the samples occurred prior their analyses. Their molar masses determined by size exclusion chromatography were probably underestimated. Due to this lack of solubility, the determination of the degree of polymerization by ^{1}H NMR spectroscopy was not performed.

Scheme 4. One-Pot Domino Synthesis of Poly(β-oxo-carbonate)s and Reagent Scope[a]



[a]M_n and PDI determined by SEC in DMF/LiBr with PS standards on crude products. SEC chromatograms of the crude products are provided in Figures S36 and S37.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

Conclusions

In this work, we have disclosed a domino approach to construct oxo-alkyl carbonate scaffolds and polycarbonates from CO_2, propargylic alcohols, and monoalcohols under mild operating conditions (pCO_2 = 1–15 bar, T = 40–80 °C). The success of the strategy was based on the design and the utilization of a binary catalyst composed of tetrabutylammonium phenolate that operated in synergy with a Ag(I) or Cu(I) salt. Remarkably, this dual catalyst (at 5 mol % loading) drove the fast, selective, and quantitative formation of exovinylene cyclic carbonates by carboxylative coupling of CO_2 to various propargylic alcohols, and it also catalyzed the alcoholysis of the *in situ* generated 5-membered cyclic carbonates, providing an efficient platform for the preparation of oxo-alkyl carbonates at high yield. Operando FT-IR spectroscopy correlated to DFT calculations provided kinetic and mechanistic insights that helped us to optimize the one-pot process via a rational comprehension of the reactivity, efficiency, and selectivity of the binary catalytic system. When this catalytic system was used on mixtures of CO_2, bis(propargylic alcohol)s, and diols, poly(β-oxo-carbonate)s with M_w up to 4300 g/mol were produced by a new domino polymerization process under mild conditions (60 °C, 15 bar). By varying the nature of the bis(propargylic alcohol) and the diol, various polycarbonates were successfully prepared, enlarging the scope of the process. Ongoing work focuses on the comprehension and the identification of the causes responsible for the moderate molar masses and the solutions to remove their hurdles.

Experimental Section

Materials. Ethynylmagnesium bromide (Acros), silver iodide, silver acetate, silver carbonate, copper chloride, copper bromide, copper iodide, zinc iodide, 2,5-hexandione, 1,4-cyclohexandione, 1,6-hexandiol, 2,5-hexandiol, 1,4-butanediol, 1,4-cyclohexandiol (cis/trans mixture), 1-butanol, propan-2-ol, 2-methyl-2-butanol, 2-methyl-3-butyn-2-ol, 3-methyl-1-pentyn-3-ol, and 3,5-dimethyl-1-hexyn-3-ol were purchased from Aldrich. CO_2 (N27) was purchased from Air Liquide, as were dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetonitrile (ACN), methanol (MeOH), diethyl ether. DMSO was dried on a 3 Å molecular sieve conditioned at 100 °C under vacuum for 24 h. All the other reagents were used as received without any further purification.

Analytical Methods. ^{1}H NMR analyses were performed on Bruker Avance 400 MHz spectrometers in DMSO at 25 °C in the Fourier transform mode. Sixteen scans for ^{1}H spectra and 512 or 2048 scans for ^{13}C spectra were recorded. Fourier transform infrared spectra were recorded using a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a transmission or with a diamond attenuated transmission reflectance (ATR) device. Spectra were obtained in transmission or ATR mode as a result of 32 spectra accumulation in the range of 4000–500 cm^{-1}, with a nominal resolution of 4 cm^{-1}.

Number-average molecular weight (M_n) and dispersity ($Đ$) of the different polymers were determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) with a Waters chromatograph equipped with two columns dedicated to the analysis of low molar mass polymers (PSS gram analytical 100 Å, separation range 300–60000 Da) and

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

a precolumn (100 Å), a dual λ absorbance detector (Waters 2487), and a refractive index detector (Waters 2414). A previously established PS calibration curve was used.

In situ IR spectroscopy experiments were conducted using a stainless steel reactor suitable for high pressure measurements (up to 400 bar) and high temperature (up to 100 °C) coupled with a FT-MIR spectrometer from Bruker, equipped with an air-cooled globar source (12 V), a KBr beam splitter, a mechanical rocksolid interferometer, permanently aligned, a diamond ATR fiber probe IN350-T (Ø 6 mm), and a liquid nitrogen-cooled mercury cadmium telluride (MCT). Single beam spectra recorded in the spectral range (670–3500 cm^{-1}) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 32 accumulated interferograms until the end of the reaction time.

Screening of Reaction Parameters for Carboxylative Coupling of CO_2 to 3-Methyl-2-butyn-3-ol. In a clean dry reactor, equipped with a magnetic rod, a manometer, and a gas inlet/outlet, 3-methyl-2-butyn-3-ol (2 mL, 20.61 mmol), tetrabutylammonium phenolate [TBA][OPh] (0.3459 g, 1.031 mmol), CuI (0.1963g, 1.031 mmol), and acetonitrile (2 mL) were introduced. The reactor was closed and placed in a silicon oil bath set heated at the desired temperature. After 30 min, CO_2 gas was added at a constant pressure. The reaction ran for 1 h after which the reactor was depressurized and placed in a water bath to cool it to room temperature. The crude reaction mixture was characterized by ^{1}H NMR spectroscopy in $CDCl_3$. For screening of the reaction parameters (*T*, solvent, catalyst), a similar protocol was applied.

Monitoring of Carboxylative Coupling of CO_2 to 3-Methyl-2-butyn-3-ol by Online FT-IR. In a clean dry reactor of 80 mL equipped with a manometer, a heating mantle, gas inlet/outlets, a mechanical stirrer, and a high pressure FT-IR probe, 3-methyl-2-butyn-3-ol (16 mL, 164.9 mmol), tetrabutylammonium phenolate [TBA][OPh] (2.7603 g, 8.225 mmol), metal salt (AgI, 8.225 mmol), and dried DMSO (16 mL) were introduced. The reactor was closed and heated to the desired temperature after which the FT-IR acquisition was launched. Then, CO_2 gas was added at a constant flow. Spectra were recorded every 2 min. Once the reaction was complete, the reactor was cooled to room temperature and depressurized. The crude mixture was recovered.

4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (2). ^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 4.79 (d, *J* = 3.8 Hz, 1H), 4.65 (d, *J* = 3.8 Hz, 1H), 1.60 (s, 6H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 158.67, 151.28, 85.92, 85.56, 27.37.

General Procedure for Synthesis of Butyl-(2-methyl-3-oxobutan-2-yl) Carbonate by Alcoholysis of αCC 2. In a clean dry glass reaction tube, equipped with a magnetic rod and a three-way stopcock, 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (0.5 g, 3.904 mmol), butanol (0.357 mL, 3.904 mmol), tetrabutylammonium phenolate [TBA][OPh] (0.0664 g, 0.1952 mmol), and DMSO (1 mL) were introduced. The reaction tube was placed in a silicon oil bath set at 25 °C. The reaction mixture was sampled after 15 min, 1 h, 2 h, and 24 h and characterized by ^{1}H NMR spectroscopy in DMSO-d_6.

General Procedure for the Domino Synthesis of Butyl-(2-methyl-3-oxobutan-2-yl) Carbonate from 2-Methyl-3-butyn-2-ol, CO_2, and Alcohol. In a stainless-steel reactor of 12 mL equipped with a magnetic bar, a manometer, and a gas inlet/outlet, 3-methyl-2-butyn-3-ol (2 mL, 20.61 mmol), tetrabutylammonium phenolate [TBA][OPh] (0.3459 g, 1.031 mmol), AgI (0.2419 g, 1.031 mmol), and 1-butanol (1.88 mL, 20.55 mmol) were introduced. The reactor was closed and placed in a silicon oil

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

bath set at 60 °C. After 30 min, CO_2 was added at a constant pressure of 15 bar. The reaction ran for 6 h after which the reactor was slowly depressurized and placed in a water bath to cool it to room temperature. The crude reaction mixture was characterized by ^{1}H NMR spectroscopy in DMSO-d_6. Then, the catalyst was removed by silica gel chromatography with CH_2Cl_2, and the product was dried under vacuum at room temperature for 24 h.

Monitoring of Synthesis of Butyl-(2-methyl-3-oxobutan-2-yl) Carbonate by Online FT-IR. In a clean dry reactor of 80 mL equipped with a manometer, a heating mantle, gas inlet/outlets, a mechanical stirrer, and a high pressure FT-IR probe, 3-methyl-2-butyn-3-ol (12 mL, 123.6 mmol), 1-butanol (11.3 mL, 123.6 mmol), [TBA][OPh] (2.0749 g, 6.182 mmol), AgI (6.182 mmol), and dried DMSO (12 mL) were introduced. The reactor was closed and heated to the desired temperature after which the FT-IR acquisition was launched and recorded every 5 min. Then, CO_2 gas was added at a constant flow. Once the reaction was complete, the reactor was cooled to room temperature and depressurized. The crude mixture was recovered and characterized by ^{1}H NMR spectroscopy in DMSO-d_6.

Butyl-(2-methyl-3-oxobutan-2-yl) Carbonate (3A).^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 4.08 (t, J = 6.6 Hz, 2H), 2.12 (s, 3H), 1.62–1.52 (m, 2H), 1.43 (s, 6H), 1.42–1.28 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.50 (C═O), 153.92 (OC═OO), 85.11, 67.90, 40.90, 30.55, 24.13, 23.33, 18.83, 13.92.

These NMR data are in agreement with those reported in the scientific literature. [38] The FT-IR-spectrum of the molecule is provided in the Supporting Information (Figure S9).

Benzyl-(2-methyl-3-oxobutan-2-yl) Carbonate (3B).^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 7.39 (s, 4H), 7.45–7.32 (m, 1H), 5.15 (s, 2H), 2.10 (s, 3H), 1.45 (s, 6H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.43 (C═O), 153.77 (OC═OO), 135.78, 128.97, 128.89, 128.60, 85.50, 69.55, 24.18, 23.34.

These NMR data are in agreement with those reported in the scientific literature. [63] The FT-IR-spectrum of the molecule is provided in the Supporting Information (Figure S12).

Isopropyl-(2-methyl-3-oxobutan-2-yl) Carbonate (3C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 4.74 (p, J = 6.2 Hz, 1H), 2.11 (s, 3H), 1.43 (s, 6H), 1.23 (d, J = 6.2 Hz, 6H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.57 (C═O), 153.32 (OC═OO), 84.95, 72.30, 24.08, 23.34, 21.86.

These NMR data are in agreement with those reported in the scientific literature. [38] The FT-IR spectrum of the molecule is provided in the Supporting Information (Figure S15).

2-Methyl-3-oxobutan-2-yl-tert-pentyl Carbonate (3D).^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 2.10 (s, 3H), 1.75 (q, J = 7.5 Hz, 2H), 1.40 (s, 6H), 1.37 (s, 6H), 0.84 (dt, J = 9.3, 7.5 Hz, 3H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.24 (C═O), 152.19 (OC═OO), 84.91, 84.35, 36.29, 25.38, 23.71, 23.16, 8.21.

Butyl-(3-methyl-2-oxopentan-3-yl) Carbonate (3E). ^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 4.08 (tt, J = 6.9, 3.4 Hz, 2H), 2.10 (s, 3H), 1.87 (dq, J = 15.0, 7.5 Hz, 1H), 1.72 (dq, J = 14.7, 7.5 Hz, 1H), 1.57 (h, J = 6.3, 5.8 Hz, 2H), 1.43 (s, 3H), 1.34 (h, J = 7.3 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H), 0.81 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.43 (C═O), 153.77 (OC═OO), 87.94, 68.46, 30.86, 28.89, 24.32, 19.68, 18.70, 14.06, 7.45.

IR-spectra of the molecule is provided in the Supporting Information (Figure S18).

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

Butyl-(3,5-dimethyl-2-oxohexan-3-yl) Carbonate (3F). ^{1}H NMR (400 MHz, DMSO-d_6) δ (in ppm) = 4.08 (td, *J* = 6.6, 3.1 Hz, 2H), 2.11 (s, 3H), 1.71 (dd, *J* = 13.2, 6.9 Hz, 2H), 1.58 (dd, *J* = 8.3, 6.3 Hz, 2H), 1.48 (s, 3H), 1.33 (q, *J* = 7.5 Hz, 3H), 0.90 (dt, *J* = 8.0, 4.4 Hz, 9H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ (in ppm) = 206.24 (C═O), 153.77 (OC═OO), 87.58, 67.83, 44.07, 30.54, 24.60, 23.85, 23.78, 20.79, 18.80, 13.92.

IR-spectra of the molecule is provided in the Supporting Information (Figure S21).

General Procedure for Domino Synthesis of Poly(*β*-oxo-carbonate)s by Terpolymerization. In a stainless-steel reactor of 12 mL equipped with a magnetic bar, a manometer, and a gas inlet/outlet, 4,4'-(ethane-1,2-diyl)bis(4-methyl-5-methylene-1,3-dioxolan-2-one) **B1** (0.3 g, 1.802 mmol) prepared following Gennen's protocol, [39] 1,6-hexandiol **D1** (0.2130 g, 1.802 mmol), tetrabutylammonium phenolate (60.5 mg, 0.1802 mmol), AgI (42.3 mg, 0.1802 mmol), and DMF (1 mL) were introduced. The reactor was closed and placed in a silicon oil bath set at 60 °C. After 30 min, CO_2 was added at a constant pressure of 15 bar. The reaction ran for 24 h, after which the reactor was depressurized and placed in a water bath to cool it to room temperature. A sample of the reaction mixture was characterized by ^{1}H NMR and ^{13}C NMR in DMSO-d_6 to determine the conversion and by SEC in order to evaluate the molecular parameters of the polymer. Then, the catalyst was removed by silica gel chromatography with CH_2Cl_2. The solvent was evaporated, and the sample washed four times with a mixture of water and CH_2Cl_2 (5:1) to eliminate DMF. The organic phase was collected, and CH_2Cl_2 was removed under vacuum at room temperature.

Associated content

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c01787.

> Methodology to calculate reactant conversion by ^{1}H NMR for the model alcoholysis of αCC; monitoring of carboxylative cyclization of 2-methyl-3-butyn-2-ol and carbonation of primary alcohol via operando FT-IR; structural NMR characterizations of reactant, crude, and isolated oxo-alkyl carbonates and oligo(oxo-carbonate)s; SEC elugrams of oligomers synthesized by the domino process; and details for DFT calculations (PDF)

Author Information

Corresponding Author

Christophe Detrembleur − Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, 4000 Liège, Belgium; **orcid.org/0000-0001-7849-6796**; Email: christophe.detrembleur@uliege.be

Authors

- Charlene Ngassam Tounzoua - Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium

- Bruno Grignard - Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium; http://orcid.org/0000-0002-6016-3317
- Antoine Brege - Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium
- Christine Jerome - Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium; http://orcid.org/0000-0001-8442-5740
- Thierry Tassaing - Institut des Sciences Moléculaires, UMR 5255 CNRS Université Bordeaux, 351, Cours de la Libération, F-33405 Talence, Cedex, France
- Raphael Mereau - Institut des Sciences Moléculaires, UMR 5255 CNRS Université Bordeaux, 351, Cours de la Libération, F-33405 Talence, Cedex, France

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Acknowledgments

The authors of Liège thank the Fonds National de la Recherche Scientifique (FNRS) and the Fonds Wetenschappelijk Onderzoek – Vlaanderen (FWO) for funding the EOS project n°O019618F (ID EOS: 30902231) and the FNRS in the frame of the FRIA project of C. Ngassam. C. Detrembleur is the FNRS Research Director. Computer time was provided by the Pôle Modélisation HPC facilities of the Institut des Sciences Moléculaires UMR 5255 CNRS – Université de Bordeaux, cofunded by the Nouvelle Aquitaine region.

References

(1) Alves, M.; Grignard, B.; Gennen, S.; Mereau, R.; Detrembleur, C.; Jerome, C.; Tassaing, T. Organocatalytic Promoted Coupling of Carbon Dioxide with Epoxides: A Rational Investigation of the Cocatalytic Activity of Various Hydrogen Bond Donors. Catal. Sci. Technol. 2015, 5 (9), 4636−4643.

(2) Alves, M.; Grignard, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Organocatalyzed Coupling of Carbon Dioxide with Epoxides for the Synthesis of Cyclic Carbonates: Catalyst Design and Mechanistic Studies. Catal. Sci. Technol. 2017, 7 (13), 2651−2684.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

(3) Fiorani, G.; Guo, W.; Kleij, A. Sustainable Conversion of Carbon Dioxide: The Advent of Organocatalysis. Green Chem. 2015, 17 (3), 1375−1389.

(4) Büttner, H.; Longwitz, L.; Steinbauer, J.; Wulf, C.; Werner, T. Recent Developments in the Synthesis of Cyclic Carbonates from Epoxides and CO2. Top. Curr. Chem. 2017, 375 (3), 1−56.

(5) Kleij, A. Green Catalytic Synthesis of Heterocyclic Structures Using Carbon Dioxide and Related Motifs. In Green Synthetic Approaches for Biologically Relevant Heterocycles; Elsevier, Inc., 2015; pp 141−162. DOI: 10.1016/B978-0-12-800070-0.00006-2.

(6) Zhang, Q.; Yuan, H. Y.; Fukaya, N.; Yasuda, H.; Choi, J. C. A Simple Zinc Catalyst for Carbamate Synthesis Directly from CO2. ChemSusChem 2017, 10 (7), 1501−1508.

(7) Zhang, Q.; Yuan, H. Y.; Fukaya, N.; Choi, J. C. Alkali Metal Salt as Catalyst for Direct Synthesis of Carbamate from Carbon Dioxide. ACS Sustainable Chem. Eng. 2018, 6 (5), 6675−6681.

(8) Arshadi, S.; Banaei, A.; Ebrahimiasl, S.; Monfared, A.; Vessally, E. Solvent-Free Incorporation of CO2 into 2-Oxazolidinones: A Review. RSC Adv. 2019, 9 (34), 19465−19482.

(9) Zhang, Q.; Yuan, H. Y.; Fukaya, N.; Yasuda, H.; Choi, J. C. Direct Synthesis of Carbamate from CO2 Using a Task-Specific Ionic Liquid Catalyst. Green Chem. 2017, 19 (23), 5614−5624.

(10) Sengoden, M.; North, M.; Whitwood, A. C. Synthesis of Oxazolidinones by Using Carbon Dioxide as a C1 Building Block and an Aluminium-Based Catalyst. ChemSusChem 2019, 12 (14), 3296−3303.

(11) Pulla, S.; Felton, C. M.; Ramidi, P.; Gartia, Y.; Ali, N.; Nasini, U. B.; Ghosh, A. Advancements in Oxazolidinone Synthesis Utilizing Carbon Dioxide as a C1 Source. J. CO2 Util. 2013, 2, 49−57.

(12) Song, J.; Liu, Q.; Liu, H.; Jiang, X. Recent Advances in Palladium-Catalyzed Carboxylation with CO2. Eur. J. Org. Chem. 2018, 2018 (6), 696−713.

(13) Luo, J.; Larrosa, I. C-H Carboxylation of Aromatic Compounds through CO2 Fixation. ChemSusChem 2017, 10 (17), 3317−3332.

(14) Yu, B.; Diao, Z. F.; Guo, C. X.; He, L. N. Carboxylation of Olefins/Alkynes with CO2 to Industrially Relevant Acrylic Acid Derivatives. J. CO2 Util. 2013, 1, 60−68.

(15) Grignard, B.; Gennen, S.; Jerő me, C.; Kleij, A.; Detrembleur, C. Advances in the Use of CO2 as a Renewable Feedstock for the Synthesis of Polymers. Chem. Soc. Rev. 2019, 48 (16), 4466−4514.

(16) Martín, C.; Kleij, A. Terpolymers Derived from Limonene Oxide and Carbon Dioxide: Access to Cross-Linked Polycarbonates with Improved Thermal Properties. Macromolecules 2016, 49 (17), 6285−6295.

(17) Yadav, N.; Seidi, F.; Crespy, D.; D'Elia, V. Polymers Based on Cyclic Carbonates as Trait d'Union Between Polymer Chemistry and Sustainable CO2 Utilization. ChemSusChem 2019, 12 (4), 724−754.

(18) Zhu, Y.; Romain, C.; Williams, C. Sustainable Polymers from Renewable Resources. Nature 2016, 540 (7633), 354−362.

(19) Kamphuis, A. J.; Picchioni, F.; Pescarmona, P. CO2-Fixation into Cyclic and Polymeric Carbonates: Principles and Applications. Green Chem. 2019, 21 (3), 406−448.

(20) Grignard, B.; Thomassin, J.; Gennen, S.; Poussard, L.; Bonnaud, L.; Raquez, J.; Dubois, P.; Tran, M.; Park, C. B.; Jerome, C.; Detrembleur, C. CO2-Blown Microcellular Non-Isocyanate Polyurethane (NIPU) Foams: From Bio- and CO2-Sourced Monomers to Potentially Thermal Insulating Materials. Green Chem. 2016, 18 (7), 2206−2215.

(21) Carre, C.; Ecochard, Y.; Caillol, S.; Averous, L. From the Synthesis of Biobased Cyclic Carbonate to Polyhydroxyurethanes: A Promising Route towards Renewable Non-Isocyanate Polyurethanes. ChemSusChem 2019, 12, 3410−3430.

(22) Poussard, L.; Mariage, J.; Grignard, B.; Detrembleur, C.; Jerome, C.; Calberg, C.; Heinrichs, B.; De Winter, J.; Gerbaux, P.; Raquez, J.-M.; Bonnaud, L.; Dubois, P. Non-Isocyanate Polyurethanes from Carbonated Soybean Oil Using Monomeric or Oligomeric Diamines to Achieve Thermosets or Thermoplastics. Macromolecules 2016, 49 (6), 2162−2171.

(23) Gennen, S.; Grignard, B.; Thomassin, J. M.; Gilbert, B.; Vertruyen, B.; Jerome, C.; Detrembleur, C. Polyhydroxyurethane Hydrogels: Synthesis and Characterizations. Eur. Polym. J. 2016, 84, 849−862.

(24) Rabnawaz, M.; Wyman, I.; Auras, R.; Cheng, S. A Roadmap towards Green Packaging: The Current Status and Future Outlook for Polyesters in the Packaging Industry. Green Chem. 2017, 19 (20), 4737−4753.

(25) Ma, S.; Liu, C.; Sablong, R. J.; Noordover, B. A. J.; Hensen, E. J. M.; Van Benthem, R. A. T. M.; Koning, C. E. Catalysts for IsocyanateFree Polyurea Synthesis: Mechanism and Application. ACS Catal. 2016, 6 (10), 6883−6891.

(26) Tang, D.; Mulder, D. J.; Noordover, B. A. J.; Koning, C. E. Well-Defined Biobased Segmented Polyureas Synthesis via a TBDCatalyzed Isocyanate-Free Route. Macromol. Rapid Commun. 2011, 32 (17), 1379−1385.

(27) Dabral, S.; Schaub, T. The Use of Carbon Dioxide (CO2) as a Building Block in Organic Synthesis from an Industrial Perspective. Adv. Synth. Catal. 2019, 361 (2), 223−246.

(28) Hu, J.; Ma, J.; Zhu, Q.; Qian, Q.; Han, H.; Mei, Q.; Han, B. Zinc(II)-Catalyzed Reactions of Carbon Dioxide and Propargylic Alcohols to Carbonates at Room Temperature. Green Chem. 2016, 18 (2), 382−385.

(29) Qiu, J.; Zhao, Y.; Li, Z.; Wang, H.; Fan, M.; Wang, J. Efficient Ionic-Liquid-Promoted Chemical Fixation of CO2 into α-Alkylidene Cyclic Carbonates. ChemSusChem 2017, 10 (6), 1120−1127.

(30) Song, Q. W.; Yu, B.; Li, X. D.; Ma, R.; Diao, Z. F.; Li, R. G.; Li, W.; He, L. N. Efficient Chemical Fixation of CO2 promoted by a Bifunctional Ag2WO4/Ph3P System. Green Chem. 2014, 16 (3), 1633−1638.

(31) Song, Q. W.; He, L. N. Robust Silver(I) Catalyst for the Carboxylative Cyclization of Propargylic Alcohols with Carbon Dioxide under Ambient Conditions. Adv. Synth. Catal. 2016, 358 (8), 1251−1258.

(32) Gu, Y.; Shi, F.; Deng, Y. Ionic Liquid as an Efficient Promoting Medium for Fixation of CO2: Clean Synthesis of α -Methylene Cyclic Carbonates from CO2 and Propargyl Alcohols Catalyzed by Metal Salts under Mild Conditions. J. Org. Chem. 2004, 69 (2), 391−394.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

(33) Falbe, J.; Bahrmann, H.; Lipps, W.; Mayer, D.; Frey, G. D. Alcohols, Aliphatic. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA, 2013; pp 1−26. DOI: 10.1002/14356007.a01_279.pub2.

(34) Magliozzi, F.; Chollet, G.; Grau, E.; Cramail, H. Benefit of the Reactive Extrusion in the Course of Polyhydroxyurethanes Synthesis by Aminolysis of Cyclic Carbonates. ACS Sustainable Chem. Eng. 2019, 7 (20), 17282−17292.

(35) Song, Q. W.; Chen, W. Q.; Ma, R.; Yu, A.; Li, Q. Y.; Chang, Y.; He, L. N. Bifunctional Silver(I) Complex-Catalyzed CO2 Conversion at Ambient Conditions: Synthesis of α-Methylene Cyclic Carbonates and Derivatives. ChemSusChem 2015, 8 (5), 821−827.

(36) Qi, C. R.; Jiang, H. F. Efficient Synthesis of β-Oxopropylcarbamates in Compressed CO2 without Any Additional Catalyst and Solvent. Green Chem. 2007, 9 (12), 1284−1286.

(37) Joumier, J. M.; Bruneau, C.; Dixneuf, P. H. Direct Access to β-Oxopropyl Carbonates from Bulky Alcohols. J. Chem. Soc., Perkin Trans. 1 1993, 50 (15), 1749−1751.

(38) Hu, J.; Ma, J.; Lu, L.; Qian, Q.; Zhang, Z.; Xie, C.; Han, B. Synthesis of Asymmetrical Organic Carbonates Using CO2 as a Feedstock in AgCl/Ionic Liquid System at Ambient Conditions. ChemSusChem 2017, 10 (6), 1292−1297.

(39) Gennen, S.; Grignard, B.; Tassaing, T.; Jerome, C.; Detrembleur, C. Polymers CO2-Sourced α-Alkylidene Cyclic Carbonates: A Step Forward in the Quest for Functional Regioregular Poly(Urethane)s and Poly(Carbonate)s. Angew. Chem., Int. Ed. 2017, 56, 10394−10398.

(40) Ouhib, F.; Grignard, B.; Van Den Broeck, E.; Luxen, A.; Robeyns, K.; Van Speybroeck, V.; Jerome, C.; Detrembleur, C. A Switchable Domino Process for the Construction of Novel CO2Sourced Sulfur-Containing Building Blocks and Polymers. Angew. Chem., Int. Ed. 2019, 58 (34), 11768−11773.

(41) Ouhib, F.; Meabe, L.; Mahmoud, A.; Eshraghi, N.; Grignard, B.; Thomassin, J.-M.; Aqil, A.; Boschini, F.; Jerôme, C.; Mecerreyes, D.; Detrembleur, C. CO2-Sourced Polycarbonates as Solid Electrolytes for Room Temperature Operating Lithium Batteries. J. Mater. Chem. A 2019, 7, 9844−9853.

(42) Ouhib, F.; Meabe, L.; Mahmoud, A.; Grignard, B.; Thomassin, J.-M.; Boschini, F.; Zhu, H.; Forsyth, M.; Mecerreyes, D.; Detrembleur, C. Influence of the Cyclic versus Linear Carbonate Segments in the Properties and Performance of CO2-Sourced Polymer Electrolytes for Lithium Batteries. ACS Appl. Polym. Mater. 2020, 2 (2), 922−931.

(43) Nakano, K.; Kamada, T.; Nozaki, K. Selective Formation of Polycarbonate over Cyclic Carbonate: Copolymerization of Epoxides with Carbon Dioxide Catalyzed by a Cobalt(III) Complex with a Piperidinium End-Capping Arm. Angew. Chem., Int. Ed. 2006, 45 (43), 7274−7277.

(44) Poland, S. J.; Darensbourg, D. J. A Quest for Polycarbonates Provided Via Sustainable Epoxide/CO2 Copolymerization Processes. Green Chem. 2017, 19 (21), 4990−5011.

(45) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. High-Activity, Single-Site Catalysts for the Alternating Copolymerization of CO2 and Propylene Oxide. J. Am. Chem. Soc. 2002, 124 (48), 14284−14285.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

(46) Inoue, S.; Koinuma, H.; Tsuruta, T. Copolymerization of Carbon Dioxide and Epoxide. J. Polym. Sci., Part B: Polym. Lett. 1969, 7, 287−292.

(47) Dabral, S.; Licht, U.; Rudolf, P.; Bollmann, G.; Hashmi, A. S. K.; Schaub, T. Synthesis and Polymerisation of α-Alkylidene Cyclic Carbonates Obtained from Carbon Dioxide, Epoxides and the Primary Propargylic Alcohol 1,4-Butynediol. Green Chem. 2020, 22, 1553−1558.

(48) Song, D.; Li, D.; Xiao, X.; Cheng, C.; Chaemchuen, S.; Yuan, Y.; Verpoort, F. Synthesis of β-Oxopropylcarbamates in a Recyclable AgBr/Ionic Liquid Catalytic System: An Efficient Assembly of CO2 under Ambient Pressure. J. CO2 Util. 2018, 27, 217−222.

(49) Song, Q. W.; Liu, P.; Han, L. H.; Zhang, K.; He, L. N. Upgrading CO2 by Incorporation into Urethanes through SilverCatalyzed One-Pot Stepwise Amidation Reaction. Chin. J. Chem. 2018, 36 (2), 147−152.

(50) Qi, C.; Huang, L.; Jiang, H. Efficient Synthesis of β-Oxoalkyl Carbamates from Carbon Dioxide, Internal Propargylic Alcohols, and Secondary Amines Catalyzed by Silver Salts and DBU. Synthesis 2010, 2010, 1433−1440.

(51) Zhao, Q.-N.; Song, Q.-W.; Liu, P.; Zhang, K.; Hao, J. Ag(I)/ (C2H5)4NCl Cooperation Catalysis for Fixing CO2 or Its Derivatives into β-Oxopropylcarbamates. Chemistry Select 2018, 3 (24), 6897−6901.

(52) Song, Q. W.; Zhou, Z. H.; Yin, H.; He, L. N. Silver(I)Catalyzed Synthesis of β-Oxopropylcarbamates from Propargylic Alcohols and CO2 Surrogate: A Gas-Free Process. ChemSusChem 2015, 8 (23), 3967−3972.

(53) Zhou, Z.; Xia, S.; He, L. Green Catalysis for Three-Component Reaction of Carbon Dioxide, Propargylic Alcohols and Nucleophiles. Wuli Huaxue Xuebao 2018, 34 (8), 838−844.

(54) Song, Q.-W.; Zhao, Q.-N.; Li, J.-Y.; Zhang, K.; Liu, P. Selective Conversion of CO2 and Switchable Alcohols into Linear or Cyclic Carbonates via Versatile Zinc Catalysis. Synthesis 2019, 51 (03), 739− 746.

(55) Zhou, Z.-H.; Song, Q.-W.; Xie, J.-N.; Ma, R.; He, L. Silver(I)Catalyzed Three-Component Reaction of Propargylic Alcohols, CO2 and Monohydric Alcohols: Thermodynamically Feasible Access to βOxopropyl Carbonates. Chem. - Asian J. 2016, 11 (14), 2065−2071.

(56) Li, J.; Song, Q.; Zhang, H.; Liu, P.; Zhang, K.; Wang, J.; Zhang, D. Synergistic Ag(I)/nBu4NBr-Catalyzed Fixation of CO2 to β-Oxopropyl Carbonates via Propargylic Alcohols and Monohydric Alcohols. Tetrahedron 2019, 75 (15), 2343−2349.

(57) Li, J.-Y.; Han, L.-H.; Xu, Q.-C.; Song, Q.-W.; Liu, P.; Zhang, K. Cascade Strategy for Atmospheric Pressure CO2 Fixation to Cyclic Carbonates via Silver Sulfadiazine and Et4NBr Synergistic Catalysis. ACS Sustainable Chem. Eng. 2019, 7 (3), 3378−3388.

(58) Grignard, B.; Ngassamtounzoua, C.; Gennen, S.; Gilbert, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Boosting the Catalytic Performance of Organic Salts for the Fast and Selective Synthesis of α-Alkylidene Cyclic Carbonates from Carbon Dioxide and Propargylic Alcohols. ChemCatChem 2018, 10 (12), 2584−2592.

Published in: ACS Sustainable Chemistry & Engineering (2020), vol. 8, n°26, pp. 9698-9710
DOI: 10.1021/acssuschemeng.0c01787
Status: Postprint (Author's version)

(59) Yang, Y.; Fan, H.; Meng, Q.; Zhang, Z.; Yang, G.; Han, B. Ionic Liquid [OMIm][OAc] Directly Inducing Oxidation Cleavage of the β-O-4 Bond of Lignin Model Compounds. Chem. Commun. 2017, 53 (63), 8850−8853.

(60) Hu, Y.; Song, J.; Xie, C.; Wu, H.; Jiang, T.; Yang, G.; Han, B. Transformation of CO2 into α-Alkylidene Cyclic Carbonates at Room Temperature Cocatalyzed by CuI and Ionic Liquid with Biomass Derived Levulinate Anion. ACS Sustainable Chem. Eng. 2019, 7, 5614−5619.

(61) Dabral, S.; Bayarmagnai, B.; Hermsen, M.; Schießl, J.; Mormul, V.; Hashmi, A. S. K.; Schaub, T. Silver-Catalyzed Carboxylative Cyclization of Primary Propargyl Alcohols with CO2. Org. Lett. 2019, 21 (5), 1422−1425.

(62) Brege, A.; Méreau, R.; McGehee, K.; Grignard, B.; Detrembleur, C.; Jerome, C.; Tassaing, T. The Coupling of CO2 with Diols Promoted by Organic Dual Systems: Towards Products Divergence via Benchmarking of the Performance Metrics. J. CO2 Util. 2020, 38, 88−98.

(63) Zhou, Z.-H.; Song, Q.-W.; Xie, J.-N.; Ma, R.; He, L.-N. Silver(I)-Catalyzed Three-Component Reaction of Propargylic Alcohols, CO2 and Monohydric Alcohols: Thermodynamically Feasible Access to Beta-Oxopropyl Carbonates. Chem. - Asian J. 2016, 11, 2065−2071.