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A Switchable Domino Process for the Construction of Novel CO₂-Sourced Sulfur-Containing Building Blocks and Polymers

Farid Ouhib⁺, *Bruno Grignard*⁺, *Elias Van Den Broeck, André Luxen, Koen Robeyns, Veronique Van Speybroeck, Christine Jerome, and Christophe Detrembleur*^{*}

Abstract: α -Alkylidene cyclic carbonates (α CCs) recently emerged as attractive CO₂-sourced synthons for the construction of complex organic molecules. Herein, we report the transformation of α CCs into novel families of sulfur-containing compounds by organocatalyzed chemoselective addition of thiols, following a domino process that is switched on/off depending on the desired product. The process is extremely fast and versatile in substrate scope, provides selectively linear thiocarbonates or elusive tetrasubstituted ethylene carbonates with high yields following a 100% atom economy reaction, and valorizes CO₂ as a renewable feedstock. It is also exploited to produce a large diversity of unprecedented functional polymers. It constitutes a robust platform for the design of new sulfur-containing organic synthons and important families of polymers.

Carbon dioxide (CO_2) is an attractive abundant, safe, and renewable carbon source for the synthesis of organic cyclic carbonates. Today, these molecules find many and diverse applications as intermediates for fine chemical synthesis, electrolytes in Li-ion batteries, polar aprotic solvents, and monomers for the preparation of world-relevant polymers such as polycarbonates and polyurethanes.^[1] The [3+2] cycloaddition of CO₂ to epoxides is the most popular and straightforward approach to five-membered cyclic carbonates^[2] and, with the recent breakthroughs in their catalyzed

[*]	Dr. F. Ouhib, ^[+] Dr. B. Grignard, ^[+] Prof. Dr. C. Jerome, Dr. C. Detrembleur
	Center for Education and Research on Macromolecules (CERM) CESAM Research Unit, University of Liège
	Sart-Tilman B6a, 4000 Liege (Belgium) E-mail:christophe.detrembleur@ulg.ac.be
	E. Van Den Broeck, Prof. Dr. V. Van Speybroeck Center for Molecular Modeling, Ghent University Technologiepark 46, 6052 Zwijnaarde (Belgium)
	Prof. Dr. A. Luxen GIGA—CRC in vivo Imaging, University of Liege Sart-Tilman B6A, 4000 Liége (Belgium)
	Dr. K. Robeyns Institute of Condensed Matter and Nanosciences (IMCN) Université Catholique de Louvain 1348 Louvain-la-Neuve (Belgium)
[+]	These authors contributed equally to this work.
Ø	Supporting information (including experimental details, supple- mentary characterizations, and computational studies) and the ORCID identification number(s) for the author(s) of this article can be found under:

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transformations,^[3] new CO₂-based organic molecules with a high degree of complexity are now accessible.^[4]

 α -Alkylidene cyclic carbonates (α CCs) are also rapidly emerging as another important class of industrially relevant CO₂-sourced cyclic carbonates.^[5] They are produced by catalytic carboxylative coupling of propargylic alcohols with CO₂.^[6] In contrast to the conventional five-membered cyclic carbonates, the presence of an exocyclic vinylic group facilitates the regioselective ring-opening of the cyclic carbonate by various nucleophiles, leading to new potentials in modern organic chemistry for the selective construction of novel molecules. The potential of αCCs for the preparation of new building blocks is enormous, but examples are still limited to β -oxocarbamates, β -oxocarbonates, β -hydroxy-1,3oxazolidin-2-ones, α-hydroxyketones, and 3-dialkylaminooxazolidin-2-ones.^[7,8] Recently, some of us demonstrated their utility for the synthesis of functional polyurethanes and polycarbonates, opening new perspectives for the design of advanced materials.^[8]

The ring-opening of α CCs by thiols is potentially attractive to drastically enlarge the scope of these CO₂-based synthons but is surprisingly unexplored. It is expected to provide new relevant sulfur-containing products for both synthetic organic (e.g. thiocarbonates) and polymer chemistries (e.g. poly(monothiocarbonates)). Thiocarbonates are notably important synthetic intermediates in organic chemistry^[9] and are used as protecting groups for thiols.^[10] Poly(monothiocarbonate)s are attractive polymers for optic applications due to their high refractive index,^[11] but also for water purification due to the strong binding ability of sulfur atom to metals.^[12] Only one article reports the reaction of thiols with α CCs, and this only by UV-activated thiol–ene addition to yield the trisubstituted ethylene carbonate **1** (Scheme 1, previous work).^[13]

In this work, we investigated the organocatalyzed thiolation of α CCs as an unprecedented source of a large palette of novel sulfur-containing organic scaffolds and polymers. We discovered that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) catalyzed the quantitative ring-opening of α CCs by various thiols, yielding either the β -oxothiocarbonate **2** or the elusive tetrasubstituted ethylene carbonate **3** in high yield (Scheme 1). Product **2** was formed extremely rapidly at room temperature, whereas **3** resulted from a novel DBUcatalyzed reaction following an on/off switchable domino process. Finally, the reactions were implemented for the synthesis of novel families of sulfur-containing polymers, including unprecedented polycyclics, with functionalities that were modulated by switching on/off the domino process.



Scheme 1. Organocatalyzed addition of thiols to CO_2 -sourced α -alkylidene cyclic carbonates and extension to functional polymers.

First, we tested the reaction of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (α CC1, Table 1, prepared by the catalyzed carboxylative coupling of CO2 to 2-methyl-3-butyn-2-ol) with benzylthiol T1 under stoichiometric conditions at room temperature in DMF without any catalyst. No reaction was observed after 24 h. In order to favor the ring-opening, DBU was added, as it had been demonstrated to facilitate the ringopening of aCCs with alcohols.^[8] Surprisingly, the unexpected tetrasubstituted ethylene carbonate 3 was quantitatively formed after only 2 h at low DBU loading (1 mol%) (Table 1, entry 2). This observation is in sharp contrast to the selective DBU-catalyzed ring-opening of α CCs by alcohols or secondary diamines that yielded β -oxocarbonates or β -oxourethanes, respectively.^[8] Replacing T1 with 2furanmethanethiol T2 also resulted in the corresponding tetrasubstituted ethylene carbonate (Table 1, entry 10) and not the expected β -oxothiocarbonate **2**. The DBU-catalyzed addition of **T1** to α **CC1** was then followed by ¹H and ¹³C NMR spectroscopy to understand the origin of this product (Supporting Information (SI), Section 2.1). After only 1 min, the cyclic carbonate was fully converted into the expected β -oxothiocarbonate **2** as the main product (91%), and the tetrasubstituted cyclic product 3 as the minor one (9%) (Table 1, entry 1). With increasing reaction time, 2 progressively disappeared in favor of 3, suggesting that 3 resulted from a rearrangement of 2. Product 3 was quantitatively recovered after 2 h, and its structure was confirmed by ¹H and ¹³C NMR spectroscopy, HR-MS, and XRD of the recrystallized product (Scheme 2C; SI Section 4.1, Table S8).

Various CO_2 -sourced αCCs (Table 1) were tested to evaluate the influence of the steric hindrance on the



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Scheme 2. A) Switchable domino process for the α CC1/T1 reaction and B) plot of the yields of 2' and 3' vs. time; C) ¹H NMR study of the DBU-catalyzed rearrangement of 2' into 3'.

selectivity of the reactions after both 1 min and 2 h of reaction. All aCCs were fully converted after only 1 min of reaction, demonstrating the impressively fast ring-opening of the cyclic carbonate (see SI Sections 2.1-2.6 for kinetics of reactions). The selectivity in 2 after 1 min slightly increased with the steric hindrance, from 91% for α CC1, to 93.5% for α CC2, and to 97% for the bulkier α CC3 (entries 1, 3, and 6, Table 1). In parallel, the selectivity in **3** after 2 h drastically decreased with the steric hindrance from 100% for α CC1, to 64% for α CC2, and 23% for α CC3 (entries 2, 4 and 7, Table 1). Bulky groups on α CCs therefore strongly slowed down the rearrangement of 2 into 3. When the reaction time was extended to 24 h, 2 was fully converted into 3 for aCC2, compared to only 47% for the bulkiest aCC3 (entries 5 and 8, Table 1). The same trend was noted for 2-furanmethanethiol T2 (entries 9–16). The substrate scope was further extended by screening the reaction of aCC1 with thiols T3 and T4 (entries 17–22, Table 1). The corresponding products 2 were produced in high yield (98-99%) after 1 min. Product 3 was formed in 58% yield with T3 when the reaction time was





$\begin{bmatrix} 0 \\ 0 \\ R^1 \\ R^2 \\ \alpha \mathbf{cc} \end{bmatrix}$	R ³ -SH DBU (1mol%) DMF, r.t.	$ \begin{array}{c} 0\\ R^1\\ R^2\\ 2 \end{array} $		acc		R ³ -SH T1 SH T1 SH T3	$ \begin{array}{c} \int_{T_2} SH \\ \\ H_{10} SH \\ T4 \\ $
Entry	αCC	Thiol	t	$Conv_{\alphaCC}$ $[\%]^{[a]}$	Conv ₂ [%] ^[a]	Yield 2 [%] ^[a]	Yield 3 [%] ^[a]
1 2	αCC1	тı	1 min 2 h	>99 >99	9.1 100	90.9 0	9.1 100
3 4 5	αCC2	ті	1 min 2 h 24 h	> 99 > 99 > 99	6.5 64 100	93.5 36 0	6.5 64 100
6 7 8	αCC3	ті	1 min 2 h 24 h	> 99 > 99 > 99	3 23 47	97 77 53	3 23 47
9 10	αCC1	Τ2	1 min 2 h	> 99 > 99	10.7 100	89.3 0	10.7 100
11 12 13	αCC2	Т2	1 min 2 h 24 h	> 99 > 99 > 99	7.3 66.6 100	92.7 33.4 0	7.3 66.6 100
14 15 16	αCC3	T2	1 min 2 h 24 h	> 99 > 99 > 99	5.3 27 56	94.7 73 44	5.3 27 56
17 18 19	αCC1	Т3	1 min 24 h 24h ^b	> 99 > 99 > 99	2 58 95	98 42 5	2 58 95
20 21 22	αCC1	Τ4	1 min 24 h 24 h ^[b]	> 99 > 99 > 99	1 3 95	99 97 5	1 3 95

Table 1: Scope of the organocatalyzed addition of thiols to α CCs.

[a] Conversions and yields determined by ¹H NMR analysis. Conv_{aCC} = conversion of α CC; Conv₂ = conversion of **2**. [b] Reaction at 80 °C. Conditions: [α CC]/[thiol] = 1/1, α CC = 4 mmol, V_{DMF} = 1 mL, room temperature.

extended to 24 h, whereas a trace amount of **3** was detected for **T4**. When the experiments were carried out at 80 °C for 24 h, product **3** was almost quantitatively formed in both cases. For all experiments, the products **2** were collected at high yields provided that the reactions were quenched after 1 min by the addition of acetic acid (10-20 mol %) which switched off the domino process.

The course of this domino process, illustrated in Scheme 2 A for the α CC1/T1 reaction, is supported by computational investigations (see SI Section 3 for details). Nucleophilic attack of the thiolate on the carbonyl group provides the metastable five-membered intermediate that ring-opens into the thiocarbonate. Proton transfer from DBUH⁺ gives the corresponding enol that tautomerizes into the thiocarbonate **2'**. This addition mode is very fast, as **2'** is formed in 91 % yield in 1 min. The process is under equilibrium, as suggested by calculations that give a free energy barrier for the back reaction of only 22.5 kJ mol⁻¹ (SI Section 3, Figure S15).

Importantly, the thiolate is also able to add to the carbon of the C=C bond (addition pathway (2)). Computational investigations suggest that this addition mode provides the corresponding carbonate anion adduct, which follows an irreversible intramolecular cyclization, aided by DBUH⁺, to provide the tetrasubstituted ethylene carbonate 3' and the release of the catalyst. A concerted mechanism might also be involved (see SI Section 3) but at this stage, it is not possible to discriminate the two mechanisms. Addition pathway (2) (stepwise or concerted) is, however, slow (complete in 2 h, Scheme 2B) compared to pathway (1) as supported by the complete kinetic analysis of the reactions (SI Sections 2.1-2.6), and in line with higher calculated free energy barriers for pathway (2) (SI Section 3). In contrast to the formation of 2' which is reversible, the reaction pathway to 3' is assumed to be irreversible. Therefore 2' is progressively fully converted into 3' in the presence of DBU, and this irreversible reaction is the main driving force for the cyclization. The formation of 2' is therefore under kinetic control, whereas the formation of 3' is under thermodynamic control. Importantly, when acetic acid was added after 1 min of reaction, the domino process was switched off. Since DBU is deactivated in this way, the reversible reaction does not occur and thus 3' is not formed; only 2' is collected. It is important to note that when alcohols were used instead of thiols in the presence of DBU under identical conditions, the domino process was not observed because the formation of the β -oxocarbonate is irreversible since alcoholates are poorer leaving groups than thiolates. The same conclusion prevails for the reaction with amines.

To further support this proposed mechanism, the thiocarbonate **2'** was synthesized according to conditions established in Table 1, entry 1. The purified compound was then dissolved in DMF to which 1 mol % of DBU was added (see SI Section 2.7). The transformation of **2'** into **3'** was then monitored at room temperature by ¹H NMR spectroscopy. Scheme 2 C shows that the thiocarbonate **2'** was progressively and fully converted into **3'** (SI Section 2.7). Also, a tiny amount of **aCC1** was detected (<1 mol %) when DBU was added to **2'** (Figure S13), supporting the reversibility of addition mode (1) (Scheme 2 A). No reaction was observed in the absence of DBU. Importantly, when two different thiocarbonates were mixed in the presence of DBU, four tetrasubstituted ethylene carbonates were collected, attesting again for the reversibility of addition mode (1) (SI Section 2.8, Figure S14).

Screening experiments with other bases of different pK_a have shown that superbases such as 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene (MTBD), and 1,5-diazabicyclo[4.3.0]non-5ene (DBN) also catalyzed the fast formation of the thiocarbonate **2'** (Table S9, SI Section 4.2). The rate of formation of **3'** was, however, slower than the reaction catalyzed by DBU. Weaker bases such as triethylamine (NEt3,), 1,4-diazabicyclo-[2.2.2]octane (DABCO), and 4-dimethylaminopyridine (DMAP) presented poor catalytic activity for the formation **2'** and did not catalyze the synthesis of **3'**. Mechanistic studies are ongoing in our laboratories in order to explain this difference of behavior.



Scheme 3. Polyadditions of dithiols with $bis(\alpha$ -alkylidene cyclic carbonate)s.

This switchable domino process was then evaluated for the construction of novel regioregular sulfur-containing polymers, by polyaddition of CO₂-sourced bis(α -alkylidene cyclic carbonate) (**BisaCC1** and **BisaCC2**, see SI Section 4.3 for their synthesis) with dithiols (**DT1** and **DT2**) (Scheme 3). The conversions, linkage selectivity, and molecular characteristics of the polymers are collected in Table 2. The DBU-

Table 2: Scope of the step-growth polyaddition of CO_2 -sourced bis(α -alkylidene cyclic carbonate)s with dithiols (see Scheme 3 for chemical structures).

Entry	BisαCC	Thiol	Catalyst	Cat. content [mol%]	Conv. [%]	$M_n [g mol^{-1}]^{[a]}$	$M_w \left[g mol^{-1} ight]^{[a]}$	$\mathcal{D}^{[a]}$	Polymer linkages ^[b]	Т _g [°С] ^[с]
1			DBU	1	>99	15 900	41 000	2.58	P1 a/P2 a : 99/1	45
2	BisαCC1	DT1	DBU	5	>99	54000	105 000	1.94	P1 a/P2 a : 99/1	47
3			FA/DBU	3/1	95	9200	17900	1.94	P1 a/P2 a : 18/82	9
4	D' 661	574	DBU	1	>99	22 000	39800	1.81	P1 b/P2 b : 99/1	126
5	BisaCC1	DT2	FA/DBU	3/1	97	21 300	45 300	2.12	P1 b/P2 b : 19/81	61
6			DBU	1	>99	15 700	32 800	2.09	P1c/P2c : 99/1	76
7	BisαCC2	DT1	FA/DBU	3/1	98	15 300	38 000	2.48	P1 c/P2 c : 30/70	32
8	BisαCC2		DBU	1	>99	75 300	103 000	1.37	P1 d/P2 d : 99/1	_[d]
9		DT2	FA/DBU	3/1	95	20800	42 700	2.05	P1d/P2d : 84/16	115

[a] Determined by size exclusion chromatography (SEC) in THF or DMF using PMMA for calibration. [b] Determined by ¹H NMR analysis in CDCl₃ or $[D_7]DMF$ at room temperature. [c] Determined by dynamic scanning calorimetry (DSC). [d] T_g higher than the degradation temperature of the polymer; conditions: [Bis α CC]/[DT]=1/1, [Bis α CC]=2 α in DMF, room temperature, 24 h.

catalyzed polyadditions provided a novel family of polymers, poly(thioether-co-cyclic carbonate)s P1a-d (Scheme 3). All polymerizations were remarkably highly selective for the thioether-co-cyclic carbonate linkages ($\geq 99\%$) at room temperature (Figures S41-48), and high conversions were noted after 24 h at a low organocatalyst content (1 mol%) (entries 1, 4, 6, and 8, Table 2). Moderate to high number average molar masses (M_n) were noted, ranging from 15700 to 75 300 g mol⁻¹. When the catalyst loading was increased, M_n also drastically increased from 15900 to 54000 gmol⁻¹ for BisaCC1/DT1 (entry 2, Table 2). For short reaction times (5 min instead of 24 h), the polymer obtained by polymerizing the BisaCC1/DT1 mixture was the poly(monothiocarbonate) P2a (90% thiocarbonate linkages) (entry 1, Table S10). These linkages were progressively fully converted into thioether-co-cyclic carbonate moieties, providing P1a, after few hours (SI Section 4.4; entries 2 and 3, Table S10; Figures S36 and S37).

Importantly, for the BisaCC2/DT2 mixture, the polymerization was extremely fast with a conversion of 95% after only 1 min, and the selective formation of P1d (thioether-cocyclic carbonate linkage of 95%) with a M_n of 11800 g mol⁻¹ (entry 1, Table S11). The rapid formation of this linkage is assumed to be the result of the high leaving group ability of the thiolate of **DT2** (Scheme 2A), which favors the cyclization. These DBU-catalyzed polymerizations thus demonstrate that the domino process is impressively fast and efficient, also for macromolecules. Although rapidly quenching the BisaCC1/DT1 polyaddition with acetic acid provided the expected **P2a**, only low M_n was obtained (4300 gmol⁻¹; entry 1, Table S10). In order to increase the M_n, the polymerization period was extended. However the domino process then occurred, leading to the transformation of the thiocarbonate linkages into thioether-co-cyclic carbonate ones (entries 2 and 3, Table S10).

With the objective to prepare polymers rich in thiocarbonate linkages and of reasonable M_n, we carried out the polymerizations in the presence of DBU (1 mol %) along with the fluorinated alcohol 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (FA, 3 mol%; Scheme 3, SI Section 4.6). Under these conditions, the series of poly(monothiocarbonate)s P2a-c with a selectivity in thiocarbonate linkages of 70-82% were prepared after 24 h (entries 3, 5, and 7, Table 2). Interestingly, by tuning the FA content, we have access to polymers with intermediate linkages content and functionality (Table S12, Figure S41). No polymerization was observed in the absence of DBU, even with 3 mol% FA. Although further mechanistic investigations are required to understand the action mode of FA, this novel strategy towards regioregular poly(monothiocarbonate)s with a potentially large scope of structures (aliphatic and aromatic) is an attractive alternative to the conventional epoxide/COS ringopening copolymerization that gives access to aliphatic polymers with limited functions.[14]

The type and content of polymer linkages has a drastic influence on the glass transition temperature (T_g) of the polymer. As a general trend, T_g significantly increased with the content of thioether-*co*-cyclic carbonate linkages. The most impressive effect on T_g was noted for the polymers

prepared with **DT2**, for instance a change in T_g from 61 °C to 126 °C with 19 and 99% of thioether-*co*-cyclic carbonate linkages, respectively (entries 5 and 4, Table 2). Interestingly, when **BisaCC2** was used, unusual hindered polycyclic structures were incorporated within the polymer backbone with an impressive impact on the thermal properties of the polymer. High- T_g polymers were formed when **BisaCC2** was polymerized with **DT2** (entries 8 and 9, Table 2, Figure S49).

In summary, we have developed a novel robust switchable domino process for the construction of important sulfurcontaining organic molecules by the organocatalyzed chemoselective addition of thiols to CO_2 -sourced α -alkylidene cyclic carbonates. Thiocarbonates but also challenging tetrasubstituted ethylene carbonates were selectively produced at high yield and at room temperature following a 100% atom economy reaction under stoichiometric conditions. This process was also exploited to prepare unprecedented regioregular sulfur-containing polymers. The "on-demand" modulation of the structure and functionality of the final product by the switching on/off of the domino process offers enormous synthetic possibilities for both organic chemistry and macromolecular engineering.

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Conflict of interest

The authors declare no conflict of interest.

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