Organocatalytic Trapping of Elusive Carbon Dioxide based Heterocycles through a Kinetically Controlled Cascade Process

Chang Qiao,[a] Alba Villar-Yanez,[a] Josefine Sprachmann,[a] Bart Limburg[a] Carles Bo[a][b] and Arjan W. Kleij*[a][c]

Dedicated to the memory of Prof. Kilian Muñiz

[a] C. Qiao, A. Villar-Yanez, J. Sprachmann, Dr. B. Limburg, Prof. C. Bo and Prof. A. W. Kleij Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 - Tarragona, Spain. E-mail: akleij@iciq.es
[b] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[c] Prof. A. W. Kleij Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

Keywords: carbon dioxide • cyclic carbonates • heterocycles • homogeneous catalysis • organocatalysis

Abstract

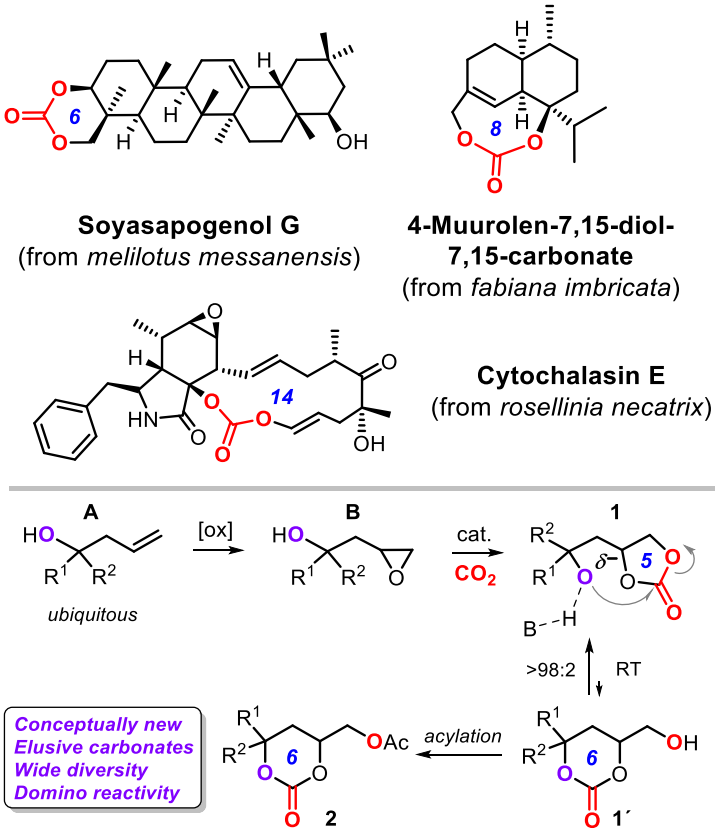
A conceptually novel approach is described for the synthesis of larger-ring cyclic carbonates derived from carbon dioxide. The approach utilizes homoallylic precursors that are converted into five-membered cyclic carbonates having a β-positioned alcohol group in one of the ring substituents. The activation of the pendent alcohol group through an N-heterocyclic base allows for equilibration towards a thermodynamically disfavored six-membered carbonate analogue that can be conveniently trapped by an acylation agent. Various control experiments and computational analysis of this manifold are in line with a process that is primarily dictated by a kinetically controlled acylation step. This cascade process delivers an ample diversity of novel six-membered cyclic carbonates in excellent yields and chemoselectivities under remarkably mild reaction conditions. This newly developed protocol helps to expand the repertoire of CO_2-based heterocycles that are otherwise difficult to generate by conventional approaches.

Introduction

The last decade has witnessed a spectacular development of a plethora of new catalytic processes that focus on the valorization of carbon dioxide (CO_2)[1] affording organic molecules of use as precursors in fine chemical,[2] pharmaceutical[3] and polymer chemistry.[4] One of the most widely applied valorization routes is undoubtedly the non-reductive transformation of CO_2. Catalyst engineering in this area has been mainly focusing on using both metal-[5] and organo-catalysts[6] for the activation of the requisite co-reactant (often cyclic ethers such as epoxides) to produce a nucleophilic intermediate species that activates CO_2 followed by the formation of the desired product. The preparation of heterocyclic targets such as cyclic carbonates,[7] carbamates[8] and ureas[9] has greatly advanced as testified by the growing complexity of these CO_2-based products.

Larger-ring, typically difficult to prepare CO_2 based heterocycles remain challenging targets (Scheme 1, top). In the area of organic carbonate synthesis, methods to generate six-membered heterocycles are scarce and often rely on stoichiometric approaches.[10] An exception is presented by the coupling reaction between oxetanes and CO_2, although to date very few catalysts have been shown to be effective for these substrates,[11] and oxetanes are much less ubiquitous than epoxides. Therefore, new concepts are required to empower the potential of such novel, functionalized heterocyclic scaffolds and widen their prospective as synthetic intermediates[12] and polymerizable monomers.[13] With this challenge in mind, we set out to design a new conceptual route towards the synthesis of six-membered cyclic carbonates from simple and accessible building blocks (Scheme 1). Homoallylic

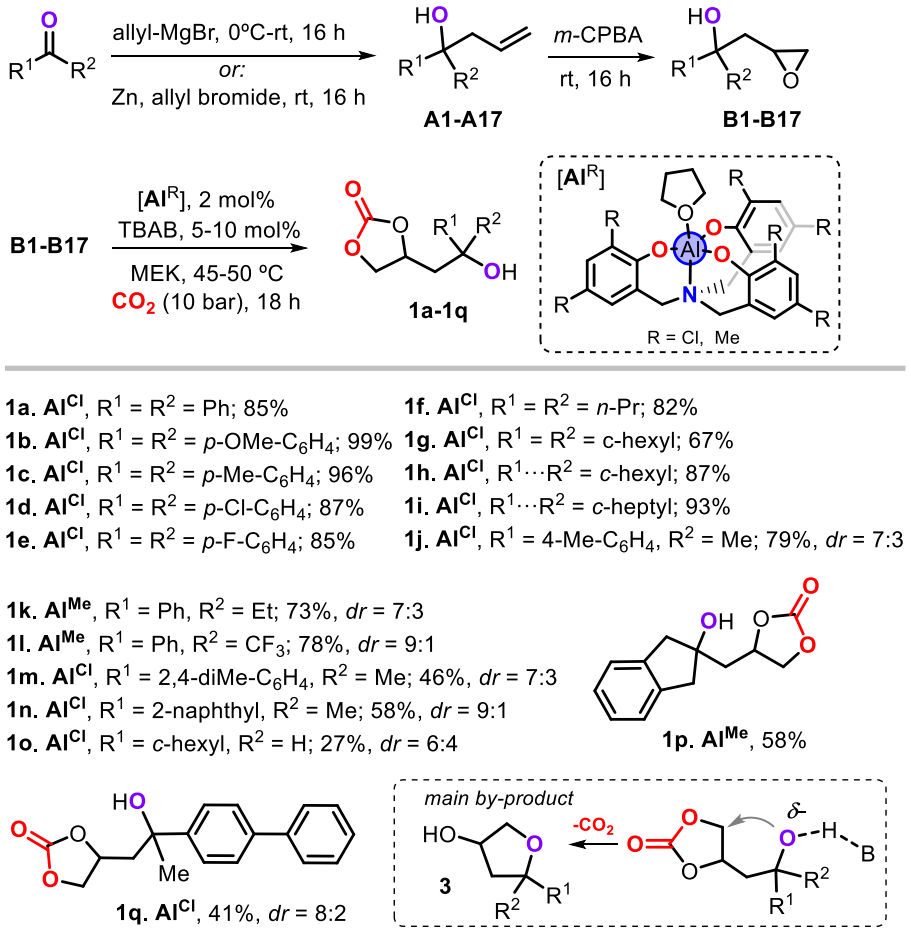
alcohols of type **A** are ubiquitous precursors and play a significant role in organic synthesis.[14] Their epoxidation directly affords substrates of type **B** that should be easily converted into intermediate 5-membered cyclic carbonate products **1**. Inspired by our previous work on substrate-controlled synthesis of organic carbonates,[15] we envisioned that the presence of a suitable organocatalyst (base) should be able to induce isomerization between carbonates **1** and **1'** with the latter being thermodynamically less stable. Selective acylation of the primary alcohol in **1'** offers then a tangible route to isolate the more elusive cyclic carbonate product **2**. Herein, we illustrate this successful, new and generally high-yielding route towards highly substituted six-membered carbonates of type **2** creating a superior diversity of such valuable heterocycles.



Scheme 1. Top: larger-ring, naturally occurring cyclic organic carbonates. Bottom: new conceptual approach towards six-membered cyclic carbonates. B stands for a base.

Results & Discussion

We first prepared a series of 5-membered cyclic carbonates of type **1** by employing various homoallylic alcohols (**A1**–**A17**) as precursors that are conveniently prepared from readily available ketones and allyl magnesium bromide. Epoxidation of these homoallylic compounds using *m*-CPBA at room temperature (rt) afforded the oxiranes **B1**–**B17** with a β-hydroxy group (see the Supporting Information, SI, for details). The oxiranes **B1**–**B17** (Scheme 2) were then used as reagents to furnish the cyclic carbonates **1a-1q** typically in good yields (with some exceptions) in the presence of CO_2 and suitable binary catalysts derived from Al-aminotriphenolate complexes $\mathbf{Al^{Cl}}$ and $\mathbf{Al^{Me}}$.[16] In some cases, significant byproduct formation occurred, and these products were identified as substituted tetrahydrofuran derivatives (see the SI for analysis details). The observed *dr* values for some of the 5-membered cyclic carbonates are similar to the ones of their respective precursors **B**, and hence supports the view that the formation of these five-membered carbonates is diastereospecific.



Scheme 2. Preparation of 5-membered carbonates **1a**–**1q** from precursors **B1**–**B17** that are prepared from homoallylic alkenes **A1**–**A17** using either $\mathbf{Al^{Cl}}$ or $\mathbf{Al^{Me}}$.

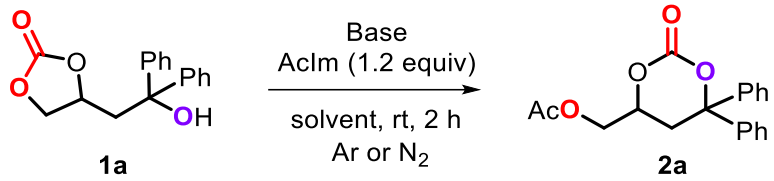
For the screening studies focusing on the preparation of six-membered cyclic carbonate **2a** (Table 1), we chose carbonate **1a** as a benchmark substrate. Various *N*-heterocyclic and standard bases were examined and acetyl imidazole (AcIm) was used as acylation reagent.[15c] The nature of the base had a significant effect on both the yield of **2a** and the overall chemo-selectivity. Among the eight bases tested, the *N*-heterocyclic ones (Table 1, entries 1, 2 and 4–6) gave the best results, with TBD (entry 1, 64%) providing comparatively the best yield of **2a**. By further variation of the solvent and the amount of TBD (entries 9–17), the best considered conditions (entry 15; 30 mol% TBD) offered an easy access to **2a** in high yield. In the absence of AcIm and by using a high loading of TBD, only tetrahydrofuran derivative **3a** could be identified (entry 17). In the absence of TBD (entry 18), no conversion of **1a** could be observed. This rt catalytic conversion of a 5- into a 6-membered cyclic carbonate is rather unique as the latter type of product is typically difficult to prepare under such mild conditions.

We then investigated the scope of this novel approach towards the formation of a wider diversity of 6-membered cyclic carbonate products (Scheme 3) by varying the R^1 and R^2 substituents. The presence of substituted aryl groups in the carbonate substrates **1a**-**1e** was well tolerated and provided smooth access to six-membered cyclic carbonates **2a**-**2e** in good to excellent yields (65-91%; gram-scale synthesis of **2a**: 1.24 g). The introduction of alkyl groups such as those present in the carbonate products **2f**-**2i** also did not pose any significant issue. Apart from the combination of two equal groups, carbonate substrates with distinct R^1 and R^2 substituents (**1j**-**1n**) were also probed. Whereas six-membered cyclic carbonates **2j**, **2k**, **2m** and **2n** were synthesized in good yields, the presence of a strongly electron-withdrawing CF_3 group (cf., attempted preparation of **2l**) changed the chemo-

selectivity in favour of the decarboxylated, *O*-acetyl protected tetrahydrofuran product **3l-Ac** which was isolated in 89% (see SI for analysis details). Finally, the *spiro*-derivative **2p** (95%) and biphenyl-based carbonate **2q** (80%) were prepared in good yields, and the identity of **2p** was further substantiated by X-ray analysis (see the inset in Scheme 3).[17]

Next, a series of control experiments were conducted to investigate the proposed role of the pendent alcohol group in substrate **1a** and the relative stability of the free alcohol carbonates (Scheme 4). In the presence of TBD only, there is no observable conversion of the 5-membered carbonate **1a** into a

Table 1. Screening conditions for the conversion of cyclic carbonate **1a** into its 6-membered congener **2a** under various conditions.[a]



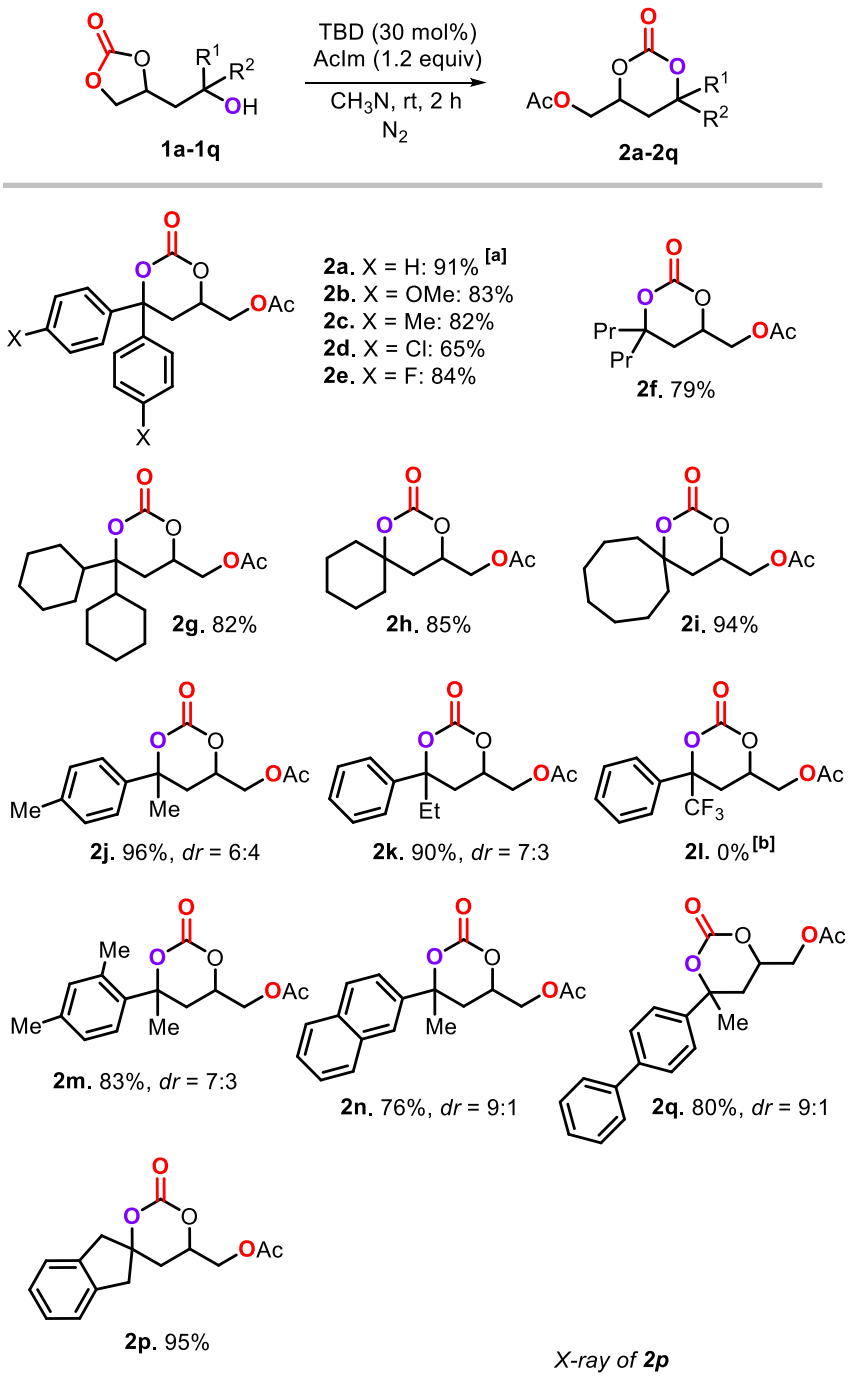
1a **2a**

Entry	Base [mol%]	Solvent	Conv. of **1a** [%][b]	Yield of **2a** [%][c]
1	TBD (20)	CH_3CN	64	64
2	DBU (20)	CH_3CN	49	49
3	KOH (20)	CH_3CN CH_3CN	100	0[d]
4	DMAP (20)	CH_3CN	8	2
5	DBN (20)	CH_3CN	43	18
6	DABCO (20)	CH_3CN	6	0
7	TEA (20)	CH_3CN	6	0
8	K_2CO_3 (20)	CH_3CN	16	0
9	TBD (20)	THF	31	31
10	TBD (20)	Et_2O	84	22
11	TBD (20)	Toluene	63	59
12	TBD (20)	DMF	15	15
13	TBD (20)	EtOH	21	3
14	TBD (20)	DCM	53	53
15	TBD (30)	CH_3CN	94	93 (91)[f]
16	TBD (50)	CH_3CN	97	97 (96)[f]
17[e]	TBD (100)	CH_3CN	>99	14[g]
18	–	CH_3CN	<1	0

[a] Reaction conditions: substrate **1a** (0.10 mmol), solvent (0.20 mL), 2 h, under Ar or N_2. [b] Conversions measured by ^1H NMR ($CDCl_3$). [c] Determined by ^1H NMR using mesitylene as internal standard. [d] An unidentified byproduct was formed. [e] In the absence of acetyl imidazole. [f] In brackets the isolated yield of **2a**. [g] Note that 5,5-diphenyl-tetrahydrofuran-3-ol (**3a**) was isolated in 14% yield, see the SI for analysis details. Abbreviations: TBD = triazabicyclodecene, DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane, TEA = triethyl amine.

6-membered one suggesting indeed that **1a** is thermodynamically significantly more stable (Scheme 4a). We separately prepared acylated **1h**-Ac and subjected this compound to the conditions that are present at the end of the cascade process (Scheme 4b). No conversion was observed pointing at the crucial role of a free alcohol group in carbonate **1h** *prior to* equilibration of the 5- to a 6-membered cyclic carbonate.

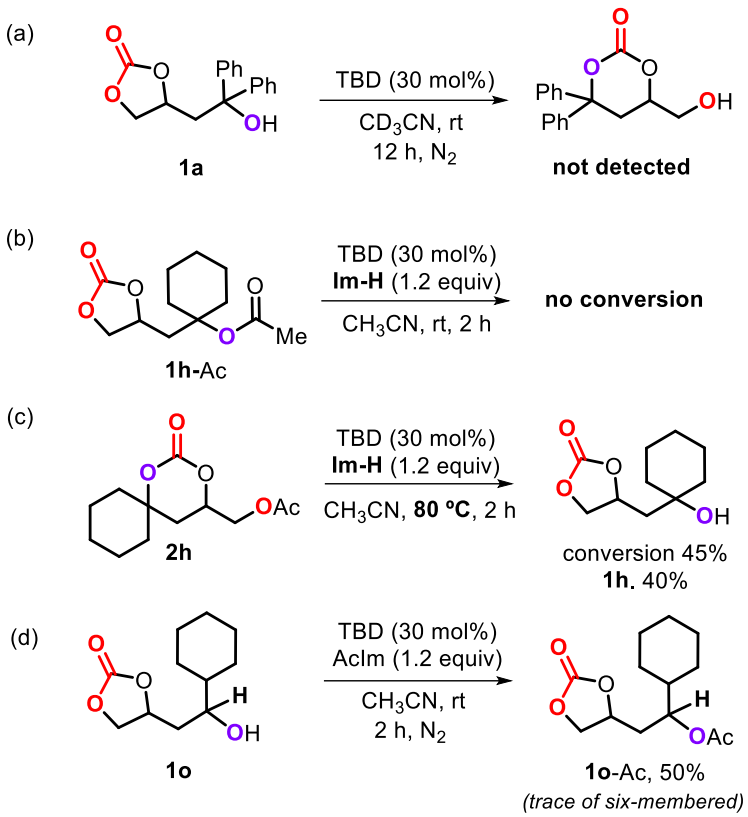
Whereas 6-membered cyclic carbonate **2h** is stable at lower temperatures, at elevated ones deprotection of the O-Ac group occurs giving the free alcohol, 5-membered cyclic carbonate **1h** as the sole carbonate product in 40% isolated yield.[18] Deprotection of **2h** therefore leads to equilibration to



Scheme 3. Scope of six-membered cyclic carbonates **2a-2q** using **1a-1q** as precursors and the reaction conditions of entry 15 in Table 1. [a] Gram-scale synthesis of **2a** using 5 mmol **1a**: yield 1.24 g, 76%. [b] The acetyl-protected tetrahydrofuran product **3l-Ac** was isolated in 89% yield, see SI for analysis data.

5-membered cyclic carbonate **1h** reinforcing the view that the free alcohol cyclic carbonate equilibrium is under thermodynamic control.

To further probe the role of the alcohol group, 5-membered cyclic carbonate **1o** comprising a secondary (instead of tertiary) OH was examined. By following the optimized conditions (Table 1, entry 15), acetylated **1o**-Ac (50%) was isolated as the major carbonate product and only a trace amount of the 6-membered carbonate was noted. This result can be anticipated as secondary alcohols should be much more susceptible towards protection largely precluding competitive carbonate equilibration to the unprotected 6-membered carbonate (cf., Scheme 1: **1** →**1´**) and subsequent acylation.



Scheme 4. Various control experiments.

To further shed light on the mechanism, density functional theory (DFT) calculations were carried out (Figure 1).[19] DFT calculations were performed using ωB97X-D functional and the 6-311G** basis set. All structures in this study were calculated with the Gaussian16 program. To obtain results as close as possible to reality, all calculations were performed at 298 K (room temperature) and an acetonitrile solvent model SMD was used. Further details are provided in the supporting information. The conversion of **1a** into **2a** was examined as a representative case.

The overall cascade process (Figure 1) can be best described as two consecutive reactions. The first one is the conversion of the five-membered carbonate **5MCC-OH** (**1a**) into the six-membered one named **6MCC-OH**, while the second step involves the protection of the alcohol of **6MCC-OH** using acetyl imidazole (AcIm) leading to the final product **2a**. The first part of the mechanism only involves **1a** and TBD with AcIm as spectator.

First, the tertiary alcohol in **5MCC-OH** is deprotonated by TBD through **TS1** obtaining **5MCC-O** and TBD-H$^+$. The alkoxide group in **5MCC-O** subsequently approaches the carbonate carbon center and generates intermediate **5MCC-Int**. From here, an isomerisation of **5MCC-Int** to **6MCC-Int1** takes place via **TS2**. This second step needs the presence of TBD-H$^+$ as to induce a closer interaction between the

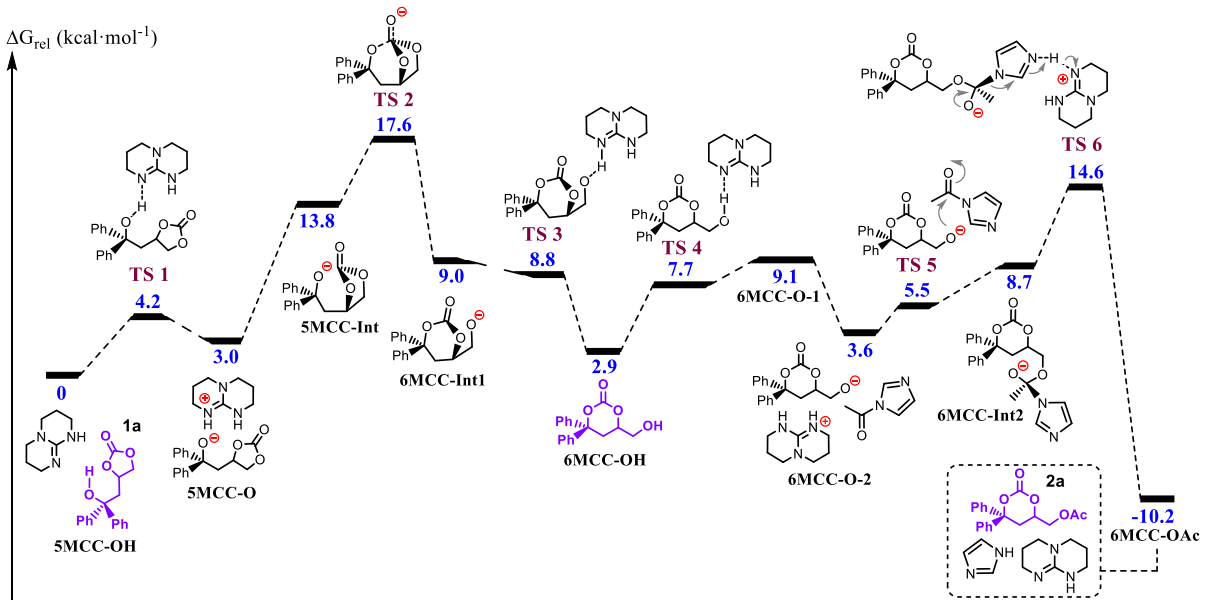


Figure 1. Relative Gibbs free energy profile in kcal·mol^{-1} for the formation of acylated six-membered cyclic carbonate **2a** from five-membered **1a** using TBD as catalyst and acetyl imidazole as acylating agent.

alkoxide and the carbonyl in **5MCC-Int** thus enabling the opening of the five-membered ring generating six-membered **6MCC-Int1**. This transformation has an energetic span of 17.6 kcal·mol^{-1} and supports the feasibility of all steps at room temperature. Then, the latter intermediate is converted into **6MCC-OH** through proton transfer from TBD-H$^+$ (**TS3**) and produces the six-membered carbonate which contains a primary alcohol. This is an important step since the conformational change while forming **TS3** positions the alkoxide group away from the carbonate carbon avoiding (to some extent) a back-reaction to **5MCC-Int1**. Importantly, **6MCC-OH** is computed to be thermodynamically significantly less stable than **5MCC-OH** (nearly 3 kcal·mol^{-1}, $K_{eq} = 7.5 \times 10^{-3}$) and corroborates with the observation that an NMR mixture of **2a** and TBD (*cf.*, Scheme 4a+c) did not show any sign of **6MCC-OH**. In order to be able to isolate the six-membered carbonate, O-protection by AcIm is thus crucial.

The second part of the cascade process describes the acylation of the primary alcohol in **6MCC-OH** (Figure 1). This O-protection using AcIm is catalyzed by TBD affording **6MCC-OAc** (**2a**) as a thermodynamically and kinetically stable product. The acylation process occurs in three steps. The first one is the deprotonation of the primary alcohol in **6MCC-OH** by TBD (via **TS4**) generating intermediate **6MCC-O-1** and TBD-H$^+$. Notably, **6MCC-Int1** is different from **6MCC-O-1** in that the alkoxide group is located nearer the carbonate carbon center of **6MCC- Int1**. This larger separation present in ternary intermediate **6MCC-O-2** and facilitated by TBD-H$^+$ allows the nucleophilic alkoxide to attack the carbonyl fragment in AcIm through **TS5** and furnishes intermediate **6MCC-Int2**. As a consequence, the carbonyl carbon of AcIm undergoes a change from sp^2 to sp^3 hybridization. Finally, TBD-H$^+$ transfers a proton to the outer nitrogen atom of the imidazole group (**TS6**) thus provoking an electronic rearrangement that allows for the generation of the final product **6MCC-OAc** (**2a**) and Im-H as by-product while regenerating TBD. The highest barrier (**TS6**) of the acylation process is located at 14.6 kcal·mol^{-1} and is substantially lower than the energetic requirement for the isomerization of **5MCC-OH** to **6MCC-OH**. This isomerization appears to be rate-limiting, and the final product **6MCC-OAc** (**2a**) is thermodynamically more stable than **1a** by 10.2 kcal·mol^{-1}.

Since all intermediates are in dynamic equilibrium, O-protection seems to make the overall cascade process irreversible at ambient temperature. To substantiate that hypothesis, we also computed the acylation of the starting carbonate **5MCC-OH** (**1a**) through the same pathway that leads to **6MCC-OAc** (**2a**). Interestingly, the acetylated carbonate **5MCC-OAc** has a substantially higher free energy than

6MCC-OAc (1.8 and –10.2 kcal·mol^{-1}, respectively) but the difference in activation barrier ($\Delta\Delta G^{\ddagger}$) of both acylation processes is markedly different (see Figure S1). At rt, the O-protection in **5MCC-OH** (having a tertiary alcohol) is energetically not competitive with the 5-to-6 carbonate isomerization/acylation cascade with a $\Delta\Delta G^{\ddagger}$ of 7.2 kcal·mol^{-1}. Therefore, key to formation of the protected product **6MCC-OAc** is a kinetic differentiation between both alcohol protection pathways allowing to selectively trap the acylated six-membered carbonate **2a** in high isolated yield.

Conclusion

In summary, we here present a unique organocatalytic manifold for the formation of elusive 6-membered heterocycles at room temperature. The six-membered cyclic carbonates that are attained this way are highly versatile and allow for the presence of several alkyl and aryl ring substituents. Computational analysis complemented by control experiments emphasize the importance of kinetic differentiation in pendent alcohol protection as a way to isolate otherwise difficult to prepare CO2 based heterocycles through a unique cascade process.

Acknowledgements

We thank the CERCA Program/Generalitat de Catalunya, ICREA, the Spanish MINECO (CTQ2017-88920-P and CTQ2017-88777-R) and AGAUR (2017-SGR-232 and 2017-SGR-290) for financial support. C. Q. acknowledges the Chinese Research Council for a predoctoral fellowship (2018-06200078) and B. L. thanks the Marie Curie COFUND/ProBIST postdoctoral fellowship program (grant agreement 754510). A.V. thanks MINECO for an FPI predoctoral fellowship.

References

[1] a) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev*. **2018**, *118*, 434-504; b) S. Liu, L. R. Winter, J. G. Chen, *ACS Catal*. **2020**, *10*, 2855-2871; c) M. B. Ross, P. de Luna, Y. Li, C.-T. Dinh, D. Kim, P. Yang, E. H. Sargent, *Nat. Catal.* **2019**, *2*, 648-658; d) A. Goeppert, M. Czaun, J.-P. Jones, G. K. Surya Prakash, G. A. Olah, *Chem. Soc. Rev*. **2014**, *43*, 7995-8048.

[2] a) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun*. **2015**, *6*, 5933; b) W. Guo, J. E. Gómez, À. Cristòfol, J. Xie, A. W. Kleij, *Angew. Chem. Int. Ed*. **2018**, *57*, 13735-13747; c) L. Song, Y.-X. Jiang, Z. Zhang, Y.-Y. Gui, X.-Y. Zhou, D.-G. Yu, *Chem. Commun*. **2020**, DOI: 10.1039/D0CC00547A.

[3] a) A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas, R. Martin, *Angew. Chem. Int. Ed*. **2018**, *57*, 15948-15982; b) W. Guo, V. Laserna, J. Rintjema, A. W. Kleij, *Adv. Synth. Catal*. **2016**, *358*, 1602-1607; c) D. U. Nielsen, X.-M. Hu, K. Daasbjerg, T. Skrydstrup, *Nat. Catal.* **2018**, *1*, 244-254.

[4] For some selected examples: a) A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chem*. **2019**, *21*, 406-448; b) B. Grignard, S. Gennen, C. Jérôme, A. W. Kleij, C. Detrembleur, *Chem. Soc. Rev*. **2019**, *48*, 4466-4514; c) S. J. Poland, D. J. Darensbourg, *Green Chem*. **2017**, *19*, 4990–5011; d) S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini, C. K. Williams, *Chem. Commun*. **2015**, 51, 6459-6479.

[5] a) R. Rajjak Shaikh, S. Pornpraprom, V. D'Elia, *ACS Catal*. **2018**, *8*, 419-450; b) J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966-1987; c) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353-1370.

[6] a) G. Fiorani, W. Guo, A. W. Kleij, *Green Chem*. **2015**, *17*, 1375-1389; b) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol*. **2017**, *7*, 2651-2684; for recent original work: c) N. Liu, Y.-F. Xie, C. Wang, S.-J. Li, D. Wei, M. Li, B. Dai, *ACS Catal.* **2018**, *8*, 9945-9957.

[7] For some illustrative, recent examples: a) G. Fiorani, M. Stuck, C. Martín, M. Martínez-Belmonte, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *ChemSusChem* **2016**, *9*, 1304-1311; b) H. Zhou, H.

Zhang, S. Mu, W.-Z. Zhang, W.-M. Ren, X.-B. Lu, *Green Chem*. **2019**, *21*, 6335-6341; c) L. Longwitz, J. Steinbauer, A. Spannenberg, T. Werner, *ACS Catal.* **2018**, *8*, 665-672.

[8] a) B. Yu, L.-N. He, *ChemSusChem* **2015**, *8*, 52-62; for some recent original examples: b) R. Yousefi, R. Yousefi, T. J. Struble, J. L. Payne, M. Vishe, N. D. Schley, J. N. Johnston, *J. Am. Chem. Soc*. **2019**, *141*, 618-625; c) J. K. Mannisto, A. Sahari, K. Lagerblom, T. Niemi, M. Nieger, G. Sztanó, T. Repo, *Chem. Eur. J*. **2019**, *25*, 10284-10289.

[9] a) M. Tamura, K. Noro, M. Honda, Y. Nakagawa, K. Tomishige, *Green Chem*. **2013**, *15*, 1567-1577; b) J. Hwang, D. Han, J. J. Oh, M. Cheong, H.-J. Koo, J. S. Lee, H. S. Kim, *Adv. Synth. Catal*. **2019**, *361*, 297-306.

[10] a) T. M. McGuire, E. M. López-Vidal, G. L. Gregory, A. Buchard, *J. CO_2 Util.* **2018**, *27*, 283-288; b) G. L. Gregory, M. Ulmann, A. Buchard, *RSC Adv.* **2015**, *5*, 39404-39408; c) M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, *ACS Catal.* **2014**, *4*, 1893-1896; d) T. Hirose, S. Shimizu, S. Qu, H. Shitara, K. Kodama, L. Wang, *RSC Adv.* **2016**, *6*, 69040-69044; using a stoichiometric iodine source: e) B. A. Vara, T. J. Struble, W. Wang, M. C. Dobish, J. N. Johnston, *J. Am. Chem. Soc.* **2015**, *137*, 7302-7305. See also: f) A. Hosseinian, S. Farshbaf, R. Mohammadi, A. Monfaredc, E. Vessally, *RSC Adv*. **2018**, *8*, 17976-17988.

[11] a) C. J. Whiteoak, E. Martin, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Adv. Synth. Catal*. **2012**, *354*, 469-476; b) J. Rintjema, W. Guo, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Chem. Eur. J*. **2015**, *21*, 10754-10762; c) B. R. Buckley, A. P. Patel, K. G. Upul Wijayantha, *Eur. J. Org. Chem*. **2014**, 474-478; d) D. J. Darensbourg, A. Horn, Jr; A. I. Moncada, *Green Chem*. **2010**, *12*, 1376-1379.

[12] a) J. Vaitla, Y. Guttormsen, J. K. Mannisto, A. Nova, T. Repo, A. Bayer, K. H. Hopmann, *ACS Catal*. **2017**, *7*, 7231-7244; b) B. D. W. Allen, C. P. Lakeland, J. P. A. Harrity, *Chem. Eur. J.* **2017**, *23*, 13830-13857. See also ref. 2b.

[13] For selected examples: a) G. L. Gregory, G. Kociok-Köhn, A. Buchard, *Polym. Chem*. **2017**, *8*, 2093-2104; b) G. L. Gregory, L. M. Jenisch, B. Charles, G. Kociok-Köhn, A. Buchard, *Macromolecules* **2016**, *49*, 7165-7169; c) P. Brignou, J.-F. Carpentier, S. M. Guillaume, *Macromolecules* **2011**, *44*, 5127-5135; d) D. J. Darensbourg, A. I. Moncada, S.-H. Wei, *Macromolecules* **2011**, 44, 2568–2576; e) D. J. Darensbourg, A. I. Moncada, *Macromolecules* **2010**, *43*, 5996-6003.

[14] For some recently developed procedures: a) M. Wadamoto, H. Yamamoto, *J. Am. Chem. Soc*. **2005**, *127*, 14556-14557; b) G.-L. Chai, B. Zhu, J. Chang, *J. Org. Chem*. **2019**, *84*, 120-127; d) Y. Zhang, N. Li, N. Goyal, G. Li, H. Lee, B. Z. Lu, C. H. Senanayake, *J. Org. Chem*. **2013**, *78*, 5775-5781.

[15] a) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán, A. W. Kleij, *Angew. Chem. Int. Ed*. **2016**, *55*, 3972-3976; b) V. Laserna, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *ACS Catal*. **2017**, *7*, 5478-5482; c) S. Sopeña, M. Cozzolino, C. Maquilón, E. C. Escudero-Adán, M. Martínez Belmonte, A. W. Kleij, *Angew Chem Int Ed*. **2018**, *57*, 11203-11207; d) R. Huang, J. Rintjema, J. González-Fabra, E. Martín, E. C. Escudero-Adán, C. Bo, A. Urakawa, A. W. Kleij, *Nat. Catal*. **2019**, *2*, 62-70; e) C. Maquilón, B. Limburg, V. Laserna, D. Garay-Ruiz, J. González-Fabra, C. Bo, M. Martínez Belmonte, E. C. Escudero-Adán, A. W. Kleij, *Organometallics* **2020**, *39*, 1642-1651.

[16] For the first use of the Al-complexes in cyclic carbonate synthesis: a) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc*. **2013**, *135*, 1228-1231; b) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2014**, *20*, 2264-2275.

[17] For details of the structure of **2p**, see CCDC-1997736.

[18] Note that beside the 5-membered carbonate product **1h** also substantial amounts of a tetrahydrofuran byproduct (cf., Scheme 2) was noted. At 110 ºC, the ratio (~ 4:1) between these products further changed in favour of the latter.

[19] For fast scans in the potential energy surface the xTB program developed by Grimme was used, see ref. 20. This program allows the scanning of one or more distances, angles and dihedral angles at the same time or sequentially, giving a general idea of each structure. Furthermore, it performs meta-dynamics simulations using the root-mean-square deviation (RMSD) in Cartesian space as

a collective variable. Full access to the computational data is provided through: http://dx.doi.org/10.19061/iochem-bd-1-171.

[20] a) S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput*. **2017**, *13*, 1989-2009. See also: b) J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys*. **2008**, *10*, 6615-6620.