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Merging Sustainability with Organocatalysis in the Formation of Organic Carbonates by Using CO₂ as a Feedstock

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The use of phenolic compounds as organocatalysts is discussed in the context of the atom-efficient cycloaddition of carbon dioxide to epoxides, forming useful cyclic organic carbonate products. The presence and cooperative nature of adjacent phenolic groups in the catalyst structure results in significantly enhanced catalytic efficiencies, allowing these CO₂ fixation reactions to operate efficiently under virtually ambient conditions. The cooperative effect has also been studied by computational methods. Furthermore, when the cycloaddition

Introduction

Carbon dioxide fixation, which is universally defined as conversion of this greenhouse gas into value-added (in)organic materials, is presently receiving enormous and increasing attention from the chemical community.^[1-6] Current emissions of carbon dioxide into the earth's atmosphere have been raising several environmental and societal concerns connected with its effect on global warming. On the other hand, carbon dioxide can also be regarded as a potentially unlimited carbon feedstock that may provide an alternative for the chemical industry because our current carbon-based feedstocks from fossil fuels are predicted to be depleted in decades to come.^[7] Carbon dioxide with sufficient purity for use as a reagent is currently available as a byproduct from many industrial processes, for example, the synthesis of ammonia and fermentation processes. Examples of successful (industrial) products that can be obtained from carbon dioxide include organic (poly)carbonates,^[8,9] methanol,^[10] and urea.^[11] Since carbon dioxide represents a kinetically and thermodynamically stable end product of all combustion processes based on organic matter, its conversion into more complicated (although useful) products involves a huge energy barrier. To reduce the kinetic hurdle, catalysis has been demonstrated to be a key technology that allows conversion of CO₂ under much milder conditions.^[12] Another aspect that may add to an overall improved process sustainability is the use of green media and reagents.^[13] In this context, organocatalysis has proven to be an innovative area in catalysis science that avoids the utilization of metal-containing species.[14-18] Organocatalysis is attracting increased attention as a result of increasingly demanding impurity specifications, which require lower amounts of metal residues to be present in end products, and thus, organocatalysis can be regarded as a highly attractive method for catalytic CO₂ conversion.

reactions are carried out on a larger scale and under solventfree conditions, further enhancements in activity are observed, combined with the advantageous requirement of reduced loadings of the binary organocatalyst system. The reported system is among one of the mildest and most effective metalfree catalysts for this conversion and contributes to a much more sustainable development of organic carbonate production; this feature has not been the main focus of previous contributions in this area.

The formation of five- and six-membered organic carbonates is a rapidly developing area of research and the most elegant way of producing these carbonates is through an atom-efficient cycloaddition of CO₂ to terminal or multiply substituted epoxides in the presence of a suitable catalyst.^[19,20] While (transition) metal catalysis is able to mediate this conversion with different degrees of success,^[21-26] organocatalyzed procedures are limited to very few examples, probably as a result of significantly reduced efficiency for substrate activation potential under mild reaction conditions compared with strong Lewis acidic metal catalysts.^[27-33] Work by Shi and co-workers has shown that phenolic compounds in combination with organic bases provide a two-component catalyst system that can be used to catalyze cyclic organic carbonate formation from epoxides and CO_2 , albeit under elevated reaction conditions (T = 100–120 °C, $p_{CO_2} = 35$ bar, 48 h) as a result of the low efficiency of this catalytic system.^[34] These conditions make this organocatalytic protocol far from ideal upon consideration of the overall sustainability. Another drawback of this system is that optimization of the catalytic efficiency is limited because more acidic phenols are involved in proton transfer to the cocatalyst

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[which in this example contains an organic base, that is, 4-dimethylaminopyridine (DMAP)], thereby inhibiting turnover because the mode of activation of the epoxide substrate is comprised of hydrogen bonding.

Other organocatalysts have also been reported for the formation of cyclic organic carbonates and related products, including ionic-liquid-based systems^[35-37] and simple ammonium halides;^[38] however, in the majority of these cases, the overall sustainability is significantly compromised by high reaction temperatures, high pressures, high catalyst loadings, or a combination thereof. This not only negatively influences the energy balance of the process, but also leads to a relatively large net output of carbon dioxide, and hence, an undesirable influence on the carbon cycle. With respect to recycling of the catalyst system, lower reaction temperatures are preferred particularly in those cases where ammonium halides are employed. Reaction temperatures that are too high may lead to fast(er) cocatalyst deactivation by Hofmann elimination; a feature that has been recently reported in detail by North and Pasquale.^[39] Therefore, with the aforementioned concerns in mind, we set out to explore new (binary) organocatalysts that are able to convert CO₂ and epoxides under highly mild reaction conditions.

Herein, we report on the development of a new, binary catalyst system comprising of commercially available (substituted) phenolic compounds combined with nBu_4NI as a cocatalyst required for the epoxide ring-opening step. These multiphenolic systems have an interesting synergistic effect, resulting

in increased hydrogen-bonding abilities towards O-donor systems (epoxides).^[40] The strong intramolecular hydrogen-bond patterns lead to large stabilization effects and different pK_a values that are potentially of use in catalytic processes.^[41] Furthermore, the presence of a quaternary ammonium iodide as the cocatalyst allows more acidic phenols to be used, higher reactivity to be attained, and hence, significantly milder reaction conditions (=lower energy input, higher catalyst stability) to be used, marking this procedure as a highly attractive, sustainable, and cost-efficient catalytic system.

Results and Discussion

The screening of various phenolic organocatalyst systems (Figure 1, **1–23**) using nBu_4NI as the cocatalyst, was carried out with 1,2-epoxyhexane as a benchmark substrate, methylethyl ketone (MEK) as a relatively green and good CO₂-solubilizing solvent.^[26] In a typical experiment, a stainless-steel autoclave was charged with 1,2-epoxyhexane, nBu_4NI cocatalyst, MEK, and mesitylene (internal standard) followed by three cycles of p_{CO_2} at 5 bar with intermediate release of the pressure and final stabilization to p_{CO_2} of 10 bar. The conversions were obtained by ¹H NMR spectroscopy using mesitylene as the internal standard for the screening are shown in Table 1. Under these





Figure 1. Organocatalyst structures 1–23.

screening conditions, the nBu_4NI cocatalyst displays no activity (Table 1, entry 1), and therefore, all activities observed are a consequence of the binary-catalyst system rather than the use of only nBu_4NI .

Initially, a series of phenols with variation of the *para*-subsituent (1–4) were tested as catalysts; a significant increase in product yield was found for the more electron-deficient system 4 compared with the parent phenol 1.^[42] Following this, a series of catechols (1,2-dihydroxybenzenes, **5–9**) were then examined.

Interestingly, in comparison with 1, an unexpected and remarkable fivefold increase in product yield was observed (75%, in the case of 5), which is significantly higher than the sum of the activity of two independent phenol units (i.e., 30%). In contrast with the series 1–4, a decrease in product yield is evident for catechols containing electron-withdrawing substituents, 7 and 8; this is ascribed to a rearrangement effect that results in significant population of the quinone form of these catechols, and thus, reduces the presence of phenolic groups. Note that the presence of an additional but distant OH group (cf., 9, 74%) does not appreciably increase the yield in this reaction when compared with 5 (74%).

A similar synergistic effect to that observed with the catechols was also noted within the series of naphthols **13–16**. The

Table 1. Screening a substrate. ^[a]	of catalysts	1– 23 whe	n using	1,2-epoxyhexane as			
	0	CO ₂	0				
	<i>n</i> Bu ─_	<i>n</i> Bu₄NI ►					
	N	/IEK, 18 h	nBc				
Catalyst	Т		Dco	Yield			
	[°C]	, [[bar]	[%] ^[b]			
-	45		10	0 ^[c]			
1	45		10	0 ^[d]			
1	25		10	3			
1	45		10	15			
2	45		10	12			
5 Л	45 45		10 10	2/ 75			
	43 25		10	75 30			
5	45		5	18			
5	45		10	75			
6	45		10	91			
7	45		10	73			
8	45		10	60			
9	45		10	74			
10	45		10	14			
11	45		10	65			
12	45		10	23			
13	45		10 10	70 24			
14	45		10	24			
15	45		10	23			
17	45		10	9			
18	45		10	0			
19	45		10	12			
20	45		10	8			
21	45		10	30			
22	25		10	63			
22	45		2	54			
22	45		5	72			
22	45		10				
22	45		10	100 (90) ^[e]			
23	45		10	/4 (/U) ^(c)			
[a] Conditions: 1,	2-epoxyhexai	ne (0.002 r	nmol), <i>i</i>	45 °C, $p_{CO_2} = 10$ bar,			
5 mol% catalyst/nE	5 mol% catalyst/nBu ₄ NI cocatalyst, MEK (5 mL), 18 h. [b] Reported yields						
are based on 'H NMR spectroscopic analysis using mesitylene as an inter-							
nal standard. [c] W	/ith only <i>n</i> Bu	u₄NI (5 mol%	%). [d] Wi	th only the catalyst			
(5.0 mol %). [e] ln b	rackets, isola	ted yields a	fter extra	ction of the product			
from the catalyst system; selectivity \geq 99% for the carbonate product.							

parent compound 13, with two adjacent phenol units, showed the highest activity (70% yield, close to that of 5, 75%), whereas 14-16 gave poorer results. Control experiments with diphenol compounds 10-12 further confirmed that the presence of two neighboring OH fragments was beneficial for catalytic activity, and 11 showed, in line with this structural prerequisite, comparable activity as that observed for 5 and 13. When the OH groups were replaced by NH_2 (17) or SH (18), only very low amounts or no product was observed, indicating the specific requirement for phenolic groups. Remarkably, a further increase in product yield could be realized by applying pyrogallol (22), which, under our screening conditions, resulted in quantitative conversion of the epoxide into its respective cyclic organic carbonate product. Again, the presence of adjacent phenolic fragments seems to be crucial for high activity because isomeric 21 (phloroglucinol) showed a markedly lower substrate conversion. Screening results obtained when using the easily prepared "bis-catechol" system 20 proved to be less effective; this can be rationalized by competitive intramolecular OH---N=CH interactions, which involve the 2-positioned phenolic groups. This effectively reduces the hydrogen-bonding ability towards substrates, leading to lower catalytic activities. In relation to this, "bis-pyrogallol" 23 showed activity lower than that observed for 22 for the same reason.

To ascertain whether the mode of activation was more general, a thiourea (19) was also screened as a potential catalyst because thioureas have been applied with prevalent success in organocatalysis due to their ability to hydrogen bond to, and thus activate, various substrate molecules.^[43] We therefore tested 19 as a catalyst in the reaction shown in Scheme 1. However, the low product yield (12%) again underlines the unique ability of phenolic groups to activate the epoxide in this reaction.

To further investigate the wider applicability of the newly developed binary-catalyst system based on 22, and the possibility of applying even milder reaction conditions (25°C), the substrate scope for compound 22 was examined (Table 2). As clearly observed, compound 22 is an effective catalyst for

Table 2. Synthesis of 4-substituted 1,3-dioxolan-2-ones when using cata- lyst 22 under optimized conditions. ^[a]						
[⊘] _R	22, CO₂ → nBu₄NI MEK, 18 h	o o R				
Substrate	Yield ^[b] [%] 25 °C	45 °C	Yield ^[c] [%]			
گر	63	100	83			
O nBu	63	100	93			
0 //Hex	42	100	91			
о Рh	27	54	52			
OPh	64	100	94			
CI	81	100	88			
ОЧ	64	83	62			
O OMe	45	93	80			
O OPh	48	96	94			
O O Ph	56	88	85			
O_4-tBuPh	45	92	90			
	51	93	81			
	22	63	51			
°	50	99	89			

[a] Conditions: epoxide (0.002 mmol), $p_{CO_2} = 10$ bar, 5 mol % catalyst/ nBu/NI cocatalyst, MEK (5 mL), 18 h. [b] Reported vields for cyclic organic carbonate products based on ¹H NMR spectroscopic analysis using mesitylene as an internal standard. [c] Isolated yields for reactions at 45 °C; selectivity \geq 99% for the carbonate product.

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Scheme 1. Gibbs energy profiles for carbonate formation catalyzed by a) iodide (in black) and b) iodide plus 22 (X = Y = OH, in blue), catechol (X = OH, Y = H, in green), or phenol (X = Y = H, in red).

a number of substrates (Table 2), giving high to quantitative yields of cyclic organic carbonate products at 45 °C and resulting in comparable activities (i.e., yields in the range 60–100%, and selectivities of more than 99%) to those reported for metal-based catalytic systems, for example, the Zn^{II}–salphen catalyst system under comparable conditions (i.e., MEK as the solvent, 45 °C, p_{CO_2} =10 bar, 18 h reaction time).^[22,23] Upon lowering the temperature to 25 °C, an expected decrease in yield was observed, although reasonable levels of product formation were still achieved. It should be noted that during the scoping experiments we were able to obtain high yields for products containing CH₂OCH₂Ph and CH₂O-4-*t*BuPh groups; the solid nature of these cyclic organic carbonate products usually limits

a recyclable catalyst if appropriately supported. After obtaining successful results when using the 22/nBu₄NI binary-catalyst system under our standard screening conditions, we further examined whether the catalyst system could be employed on a larger scale. Reactions were performed at 25 and 45 °C in neat propylene oxide (1 g, 17 mmol scale, compared with 2 mmol in the screening experiments) by using a reduced loading of only 2.0 mol% of the binary-catalyst system. After 18 h, the isolated yield of propylene carbonate was very high (93–96%, Table 3), suggesting that quantitative conversion of the epoxide had taken place. When the reaction in

sion of the epoxide had taken place. When the reaction in neat propylene oxide was performed with only **22** or $nNBu_4NI$ (2 mol%) for 18 h, conversions of 0 and 26% were obtained, respectively, which are significantly lower than the isolated yields obtained for the binary-catalyst system. Shorter reaction

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the opportunity for full conversion of these epoxides under neat conditions unless high temperatures required for "catalysis in the melt" are applied, and therefore, the use of a solvent (MEK) can be beneficial in these cases.

Pure isolated organic cyclic carbonate products could be easily obtained by simple solvent extraction from the crude reaction residue. After removal of the solvent under vacuum, the cyclic organic carbonate was extracted by using toluene/heptane $(3:1 \ v/v)^{[44]}$ and ¹H and ¹³C NMR spectra for all isolated compounds were obtained (see the Supporting Information), and additionally IR spectroscopy further confirmed the formation of these carbonate structures.

The residue remaining after extraction of the cyclic organic carbonate product contained the original binary-catalyst system, as supported by ¹H NMR spectroscopy. To gain insight into the stability of the catalyst system, the residue was then reused as a catalyst in a second run. It was found that indeed this residue was catalytically active, but resulted in a somewhat lower isolated yield (78%) than that observed in the first catalytic run (90%). Therefore, the 22/nBu₄NI binary catalyst system may show potential as a recyclable catalyst if appropri-

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Table 3. 22/nNBu	Synthesis of pro ₄NI system in ne Me	pylene carbona at propylene ox ○ 22, CO ₂ ∩Bu₄NI	te when using the bir ide. ^[a]	nary-catalyst		
Т	t	22	nBu ₄ NI	Yield		
[°C]	[h]	[mol%]	[mol %]	[%] ^(b)		
45	18	2.0	-	0		
45	18	-	2.0	26		
45	18	2.0	2.0	93		
25	18	2.0	2.0	96		
45	1	2.0	2.0	43		
45	2	2.0	2.0	65		
45	3	2.0	2.0	78		
45	4	2.0	2.0	84		
25	6	2.0	2.0	69		
[a] Conditions: propylene oxide (17 mmol), $p_{CO_2} = 10$ bar (at $t = 0$ h), 2.0 mol% catalyst/nBu ₄ Nl cocatalyst, no co-solvent. [b] Isolated yields; selectivity \geq 99% for the carbonate product.						

times were then investigated and the pressure drop in the reactor was monitored over time (Figure 2). At 45 °C, after only 4 h the isolated yield of product was marginally lower (84%) than that obtained after 18 h (93%). At 25 °C, as expected, after 6 h the isolated yield of the cyclic carbonate was lower (69%). Isolated yields obtained after 1, 2, and 3 h at 45 °C were



Figure 2. Pressure development over time at 25 and 45 °C for the conversion of propylene oxide into its carbonate. See Table 3 for details and isolated yields.

also obtained (Table 3) and followed a reverse trend of CO_2 uptake observed during the reaction (Figure 2). These results indicate that under neat conditions the **22**/nBu₄NI binary-catalyst system is more active than when used with a co-solvent and marks this system as a rare example of an organocatalyst system that is active under mild conditions for this cycloaddition reaction.

The mechanism for carbonate formation in MEK was studied computationally by DFT (B3LYP) calculations. Preliminary calculations (see the Supporting Information) indicated no involvement of the R_4N^+ cation, which was consequently neglected from the most elaborate calculations reported herein. With iodide as the only catalyst (Scheme 1 a, energy profile in black), nucleophilic addition, epoxide ring opening, and CO_2 addition take place simultaneously in **TS1**, with a free energy of 38.9 kcal mol⁻¹ (1 cal = 4.2 J). Afterwards, the transition state for the carbonate ring-closure step (**TS2**) has an energy of 30.8 kcal mol⁻¹ above the separate reactants. The rate-limiting step is thus marked by **TS1** and the barrier of 38.9 kcal mol⁻¹ is consistent with a sluggish reaction under these experimental conditions.

This mechanism changes when a phenol derivative is introduced as the catalyst in addition to iodide (Scheme 1b). A new intermediate $I1_{X,Y}$ appears, resulting from ring opening of the epoxide upon interaction with the two catalysts. The largest effect is observed for 22 (blue profile in Scheme 1b), which is discussed herein in some detail. In this case, one proton from the central hydroxyl group of 22 is transferred to the alkoxylic center, resulting from the ring opening of the epoxide. The OH distances for this O-H-O fragment are 1.50 and 1.03 Å in $I1_{OH,OH}$; this shows a strong hydrogen-bonding interaction. The newly formed OH group is stabilized by another OH group of 22, while the remaining OH group stabilizes the oxygen atom of the phenoxide. Intermediate I1_{OH,OH} is formed from the reactants through $TS1_{OH,OH}$, with a relative energy of 27.3 kcal mol⁻¹. Afterwards, CO₂ addition takes place through TS2_{OH,OH}, with a relative energy of 29.7 kcalmol⁻¹. Catalyst 22 then dissociates from the reacting system, which reverts to **I1** and evolves to products through TS2. All attempts to keep 22 associated to the system after TS2_{OH,OH} resulted in species such as 12_{0H.0H} (Scheme 2) with higher free energies than the corresponding ones in Scheme 1. The key result from the full energy profile is that the highest energy point is TS2_{OH,OH}, with an energy of 29.7 kcal mol⁻¹ above the separate reactants. This is much lower than 37.7 kcalmol⁻¹ required for the mechanism without 22 and explains the catalytic role of this molecule. It is also worth noting that the main role of 22 is the stabilization of intermediate I1_{OH.OH}, and the two transition states connected to it, but it does not assist the ring-closure step.

As shown in Scheme 2, the three hydroxyl groups of **22** participate in the stabilization of $I1_{OH,OH}$. Thus, replacement by hydrogen of one or two of them (that is, replacing **22** with catechol or phenol) should have consequences on the rate of the reaction. This is indeed the trend observed in the profiles in



Scheme 2. Proposed catalytic cycle when using binary catalyst 22/nBu₄NI.

Scheme 1, the energies associated to the highest energy points **TS2**_{OH,H} and **TS2**_{H,H} are 32.9 and 37.7 kcal mol⁻¹, respectively. This is fully consistent with the yields obtained with catalysts 1, 5, and 22 at 45 °C and 10 bar of CO₂ of 15, 75, and 100% respectively, as shown in Table 1. The high computed barriers for all processes are also consistent with the requirement of high CO₂ pressure and more than one equivalent of catalyst and cocatalyst. These computational results show that the key role of the OH groups in 22 is in stabilizing intermediates and transition states by means of inter- and intramolecular hydrogen bonds,^[40,41] and provide a mechanistic picture that explains all of the experimental observations.

Conclusions

Catechol and/or pyrogallol (22) scaffolds are excellent organocatalysts for the preparation of various cyclic organic carbonates from epoxides and carbon dioxide as starting materials. The occurrence of synergistic effects translates into a catalytic system with a favorable energy balance and allows carbon dioxide fixation into useful organic matter under very mild reaction conditions. The binary organocatalyst system 22/nBu₄NI is a powerful catalyst with ample substrate scope under very mild reaction conditions (25–45 °C, $p_{CO_2} = 10$ bar, 2–5 mol% catalyst, and no need for a solvent) compared with the current state of the art. It therefore represents a new attractive organocatalytic protocol that can be operated under conditions that are desirable from an energy and CO₂-emission point of view, adding up to a higher degree of sustainability. Furthermore, this work also demonstrates that commercially available 22 may hold promise as a catalyst that can also activate other O- and N-containing substrates through hydrogen bonding. Currently we are designing other types of polyphenolic structures useful as hydrogen-bond activators in the context of CO₂ conversion.

Experimental Section

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General: MEK and carbon dioxide (purchased from PRAXAIR) were used as received without further purification or drying prior to use. All phenolic compounds (except for **20** and **23**) were commercially purchased from Sigma Aldrich and used without any further purification. Compound **20** was previously reported and prepared as such.^[45] The synthesis of **23** is reported herein. The organic products **24a**–**n** have been reported previously.^[46–52] ¹H NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. Elemental analysis was performed by the Unidád de Análisis Elemental at the Universidad de Santiago de Compostela. MS analysis was performed by the Research Support Group at the ICIQ.

Typical catalytic experiment: A solution of nBu_4NI (5 mol%, 37.6 mg), **22** (5 mol%, 12.6 mg), 1,2-epoxyhexane (0.002 mmol, 200 mg), and mesitylene (0.002 mmol, 244 mg) in MEK (5 mL) were added to a stainless-steel reactor. Three cycles of pressurization and depressurization of the reactor (with $p_{CO_2} = 5$ bar) were carried out before finally stabilizing the pressure at the required pressure. The reactor was then heated to the required temperature and left stirring for a further 18 h. An aliquot of the solution was then ana-

lyzed by means of ¹H NMR spectroscopy using [D₆]DMSO as the solvent and the yield was determined by using mesitylene as the internal standard. Isolated yields and ¹H/¹³C{¹H} NMR spectra of all products synthesized at 45 °C are reported in Table 2 and were obtained by removing the solvent, mesitylene, and unreacted substrate under vacuum. The residue was then dissolved in toluene (10 mL) and heptane was added until a precipitate formed. The mixture was then filtered and the solvent was removed from the filtrate to yield the pure, substituted, organic cyclic carbonate. 4-(Hydroxymethyl)-1,3-dioxolan-2-one required a slightly different extraction from the catalytic system due to its polarity: after the initial vacuum step, the residue was dissolved in chloroform (20 mL) and heptane (4 mL) was added. The mixture was then filtered and the solvent was removed under vacuum. Acetone (0.5 mL) and diethyl ether (25 mL) were added to this residue. After 3 h at -30 °C, the mixture was filtered and the solvent was removed from the filtrate to yield pure 4-(hydroxymethyl)-1,3-dioxolan-2-one (24g). The identity of each of the organic cyclic carbonate products was confirmed by comparison to the literature values previously reported (see also the Supporting Information).

Typical NMR spectroscopy data for organic cyclic carbonate product: 4-Methyl-1,3-dioxolan-2-one: Yield: 83%; ¹H NMR (CDCl₃, 500 MHz): δ = 4.90–4.82 (m, 1H; OCH₂CHO), 4.56 (dd, ³J(H,H) = 8.4, 7.8 Hz, 1H; OCH₂CHO), 4.03 (dd, ³J(H,H) = 8.4, 7.2 Hz, 1H; OCH₂CHO), 1.50 ppm (d, ³J(H,H) = 6.3 Hz, 3H; CHCH₃); ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ = 155.1 (C=O), 73.6, 70.7, 19.4 ppm. For complete data for all other products from Table 2, see the Supporting Information.

Synthesis and characterization of compound 23: A solution of (R,R)-1,2-diphenyl-ethanediamine (117.4 mg, 0.553 mmol) in iPrOH (20 mL) was combined with 2,3,4-trishydroxybenzaldehyde (232.0 mg, 1.51 mmol) and briefly heated to reflux. After cooling to ambient temperature, a yellow solution was obtained that upon further cooling precipitated a yellow solid. Filtration afforded 23, which was dried in air and obtained as a yellow powder (248.7 mg, 74%, corrected for *i*PrOH inclusion). ¹H NMR ([D₆]DMSO, 500 MHz): $\delta\,{=}\,13.73$ (brs, 2H; OH), 9.45 (brs, 2H; OH), 8.35 (brs, 2H; OH), 8.26 (s, 2H; CH=N), 7.31-7.23 (m, 7H; ArH), 7.20-7.16 (m, 2H; ArH), 6.59 (d, ³J(H,H) = 8.5 Hz, 2H; ArH), 6.25 (d, ³J(H,H) = 8.4 Hz, 2H; ArH), 4.98 ppm (s, 4H; NCH₂CH₂N); ¹³C{¹H} NMR ([D₆]DMSO, 125 MHz): $\delta = 166.5$, 152.6, 149.9, 140.8, 132.9, 128.6, 128.2, 127.7, 123.4, 111.8, 107.6, 77.2 ppm; HRMS (MALDI+, dctb): m/z calcd for 485.1713 [M]⁺; found: 485.1750; elemental analysis calcd (%) for C₂₈H₂₄N₂O₆·2*i*PrOH·0.5H₂O: C 66.54, H 6.73, N 4.56; found: C 66.90, H 6.87, N 4.85. The presence of iPrOH in the product was confirmed by both ¹H and ¹³C{¹H} NMR spectroscopy analysis.

Computational details: All calculations were performed with the Gaussian 09 package^[53] of programs with the hybrid B3LYP functional.^[54] The basis set was the ECP-adapted SDDALL^[55] with a set of polarization functions for I,^[56] the all-electron 6-31G(d,p)^[57] for H and C, and the 6-31 + G(d,p)^[58] for O. Full optimization of geometry was performed in MEK by using the continuum SMD model^[59] without any symmetry constraints, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or transition states. Each transition state was relaxed toward reactant and product by using the vibrational data to confirm its nature. The zero-point, thermal, and entropy corrections were evaluated to compute enthalpies and Gibbs free energies (*T*=298 K, *p*=1 bar).

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FULL PAPERS

C. J. Whiteoak, A. Nova, F. Maseras,* A. W. Kleij*

Merging Sustainability with Organocatalysis in the Formation of Organic Carbonates by Using CO₂ as a Feedstock



In a fix: A new organocatalytic method for organic carbonate synthesis is reported and allows attractive conditions $(25 \degree C, 10 \text{ bar, no solvent})$ to be used (see picture). Cyclic carbonates produced from CO₂ and epoxides are isolated in high yields. The mild nature of this process increases the overall process sustainability for this type of widely studied carbon dioxide fixation process.