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Carbonate Phosphonium Salts as Catalysts for the Transesterification of Dialkyl Carbonates with Diols. The Competition between Cyclic Carbonates and Linear Dicarbonate Products

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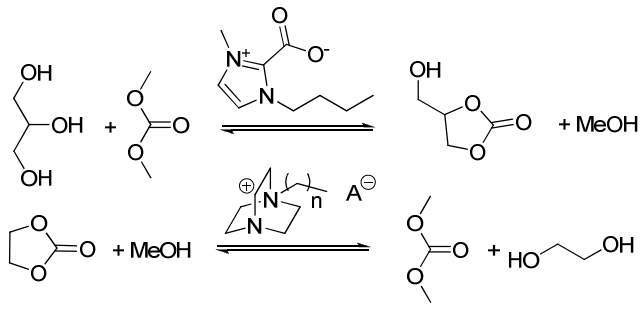
ABSTRACT. At 90-120 °C, in the presence of methylcarbonate and bicarbonate methyltrioctylphosphonium salts as catalysts ([P_{8881}][A]; [A] = $MeOCO_2$ and $HOCO_2$), the transesterification of non-toxic dimethyl- and diethyl-carbonate (DMC and DEC, respectively) with 1,X-diols ($2 \leq X \leq 6$) proceeds towards the formation of cyclic and linear products. In particular, 1,2-propanediol and ethylene glycol afford propylene- and ethylene-carbonate with selectivity and yields up to 95 and 90%, respectively; while, the reaction of DMC with higher diols such 1,3-butanediol, 2-methyl-1,3-propanediol, 1,3-propanediol,2,2-dimethyl 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol produce linear C_8-C_{10} dicarbonates of general formula MeOC(O)O~~~OC(O)OMe as the almost exclusive products. Of note, these dicarbonate derivatives are not otherwise accessible in good yields by other conventional base catalyzed methods. Among 1,3-diols, the only exception was 2-methyl 2,4-pentandiol that yields the corresponding cyclic carbonate, *i.e.*4,4,6-trimethyl-1,3-dioxan-2-one. In no one case, polycarbonates are observed. Such remarkable differences of product distributions are ascribed to the structure (branching and relative position of OH groups) of diols and to the role of cooperative (nucleophilic and electrophilic) catalysis which has been proved for onium salts. The investigated carbonate salts are not only effective in amounts as low as 0.5 mol%, but they are highly stable and recyclable.

KEYWORDS: Dialkyl carbonates, transesterification, carbonate exchanged phosphonium salts, cyclic carbonates, organocatalysis

INTRODUCTION

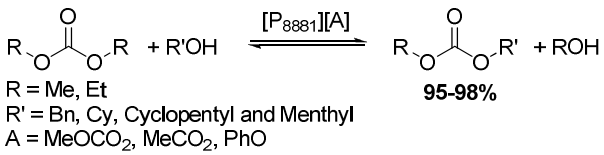
In the past two decades the growing demand for eco-friendly organic carbonates as intermediates for pharmaceuticals, lubricants, fuels, solvents, and polymers, has triggered a massive research activity to devise transesterification procedures for the synthesis of both diaryl and dialkyl carbonates.[1,2] Patent and open literature offer a plethora of catalytic methods to accomplish these processes. Catalysts more often include bases such as phosphines and tertiary amines, alkali metal hydroxides, alkoxides, halides, and inorganic carbonates, alkali metal exchanged faujasites, and hydrotalcites,[2-3] but acid compounds (sulfonated Amberlyst resins and Zn-based MOF) are reported as well.[4] A great potential is envisaged also by versatile organocatalysts such as ionic liquids (ILs); yet, the use of these compounds represents a largely unexplored area. Among few reported examples, two recent remarkable ones are shown in Scheme 1 where the synthesis of glycerol carbonate and dimethyl carbonate is described via transesterification processes catalyzed by task-specific (basic) ILs as 1-*n*-butyl-3-methylimidazolium-2-carboxylate (top) and DABCO-derived systems (bottom), respectively.[5,6]



Scheme 1. Transesterifications of organic carbonates catalyzed by ionic liquids

Even more recently, we also discovered that new weakly basic phosphonium salts synthesized in our laboratories, namely methyltrioctylphosphonium methyl carbonate (**1a**: $[P_{8881}][MeOCO_2]$) and methyl trioctylphosphonium bicarbonate (**1b**: $[P_{8881}][HOCO_2]$), act as efficient transesterification

catalysts as well as catalytic precursors.[7] In this case, the reaction of both dimethyl and diethyl carbonate (DMC and DEC, respectively) with model primary and secondary alcohols proceeds towards the selective formation of unsymmetrical dialkyl carbonates (Scheme 2).



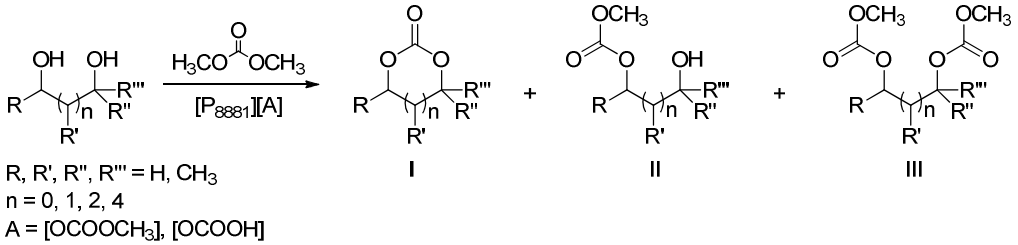
Scheme 2. Synthesis of unsymmetrical dialkyl carbonates via transesterifications catalyzed by phosphonium salts.

Major advantages associated with compounds **1a-b** include the following. i) An excellent catalytic activity. Beyond transesterification processes, salts **1a-b** can be used for fundamental C-C bond forming reactions such as Michael, Henry, and Baylis-Hilman transformations, where they exhibit performances comparable to those of organic superbases such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and phosphazene P1–*t*Bu.[7,8] ii) The availability of a green method for their preparation. The key step of the synthesis of **1a-b** involves a simple halide-free methylation of an alkyl phosphine with non-toxic dimethyl carbonate (DMC).[8] iii) Versatility. Carbonate onium salts, particularly **1a**, serve as catalysts as such, or they may be anion exchanged with a variety of acids (HA: A=NO_3, AcO, CF_3CO_2,TsO, $ArCO_2$, etc.) to generate libraries of derivatives ([P_{8881}][A]) in a highly pure form. By-products of these reactions are only MeOH and CO_2. iv) finally, compounds **1a-b** show a good thermal stability.

As a part of our long-standing interest for the implementation of green protocols based on organic carbonates and ILs as organocatalysts,[1a,2,7-8,9] we decided to further explore the behavior of carbonate salts **1a-1b** to catalyze the transesterification of DMC and DEC with different 1,n-diols (n = 2, 3, 4, and 6). This research was a significant extension of our previous investigation on the subject (Scheme 2),[7] since it was not only aimed at investigating the feasibility of the reaction, but also at studying possible effects of the chain length and the degree of substitution of the carbon backbone of diols. For this reasons, a substantial number of substrates including 1,2-diols such as 1,2-propane- and 1,2-ethane- diol (**2** and **3**, respectively), 1,3-diols such as racemic 1,3-butanediol

(**4**), 2-methyl-1,3-propanediol (**5**), 1,3-propanediol (**6**),2,2-dimethyl 1,3-propanediol (**7**), and 2-methyl 2,4-pentandiol (**8**), and other 1,n-diols such as 1,4-butanediol (**9**), and 1,6-hexanediol (**10**) were used.

This paper demonstrates that, in the presence of salts **1a-b**, reactions proceeded with complete conversion towards the formation of transesterification products, *i.e.* cyclic and linear carbonates (I, II and III, respectively; Scheme 3 illustrates the model case of DMC).



Scheme 3. The transesterification of dimethyl carbonate with diols catalysed by carbonate phosphonium salts.

Even more interestingly, depending on the substrate and reaction conditions, experiments proved that the product distribution could be largely controlled: the selectivity could be shifted from cyclic to linear di-carbonates (I and III), which were isolated in good-to-excellent yields (70->90%).

Beside the effect of diol structures, other reaction parameters such as the reactant molar ratio and the catalyst loading were examined. This investigation prompted some general considerations on the synthetic scope of the method and on the mechanism at the basis of the competition between ring-closing transesterification to yield carbonates I, and the formation of linear mono- (II) and di-carbonates (III).

RESULTS

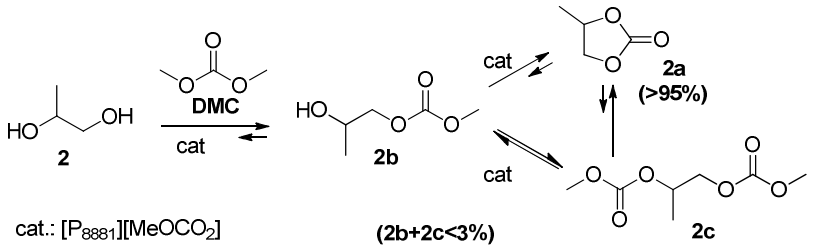
Catalysts. Methyltrioctylphosphonium methylcarbonate (**1a**: $[P_{8881}][MeOCO_2]$) and methyltrioctylphosphonium bicarbonate (**1b**: $[P_{8881}][HOCO_2]$) were used as model organocatalysts. These compounds were prepared through a procedure implemented by our group.[8] Accordingly, at 150 °C, *n*-trioctyl phosphine (20.8 g) was initially methylated by DMC (30 mL) in the presence of MeOH as a co-solvent (30 mL). This allowed to isolate compound **1a** in quantitative yield. In a second step, compound **1a** (3.0 g) was mixed with water (1.0 mL) at 40 °C. A rapid hydrolysis of

the methylcarbonate anion ($MeOCO_2$) took place with the formation of salt **1b** (>99%) and the release of MeOH as a co-product. Both salts **1a** and **1b** were stable colorless liquids at rt, and were used as such without any further purification. (Additional synthetic details are in the experimental section).

1,2-Diols. The study of transesterification reactions started by using 1,2-diols such as 1,2-propanediol and 1,2-ethanediol (**2** and **3**, respectively). The reaction of **2** with DMC was initially examined: effects of the temperature, the catalyst loading, and the DMC:**2** molar ratio, respectively, were explored.

A mixture of **2** (837 mg, 11.0 mmol), DMC and $[P_{8,8,8,1}][OCO_2Me]$ in a 1: 20: 0.01 molar ratio, respectively, was set to react at three different temperatures of 90, 70 and 50 °C, for 6 hours. Then, under the same conditions, two additional experiments were performed at 90 °C: in the first, the catalyst amount was halved (**2**:$[P_{8,8,8,1}][OCO_2Me]$=1:0.005 molar ratio), while in the second one, a blank reaction was run in the absence of the onium salt.

At intervals, samples of the reaction mixtures were collected and analyzed by ^1H NMR and GC/MS. Cyclic propylene carbonate (4-methyl-1,3-dioxolan-2-one, **2a**) was by far, the major product (>95%). Two byproducts were detected in trace amounts (total: ≤3%): these two compounds were supposed to be the corresponding mono- and di-transesterified derivatives (**2b** and **2c**, respectively). Scheme 4 offers a plausible pattern of the transesterification equilibria involved in the overall process.



Scheme 4. Transesterification of 1,2-propanediol with DMC catalyzed by $[P_{8,8,8,1}][OCO_2Me]$

NMR evidence was consistent with this hypothesis. However, since products **2b** and **2c** were observed in a very low concentration, they could not be isolated and any study of possible interconversions between **2a**, **2b**, and **2c** was of no practical implementation.

The conversion profiles of **2** at different temperatures and at different catalyst loadings are reported in Figure 1.

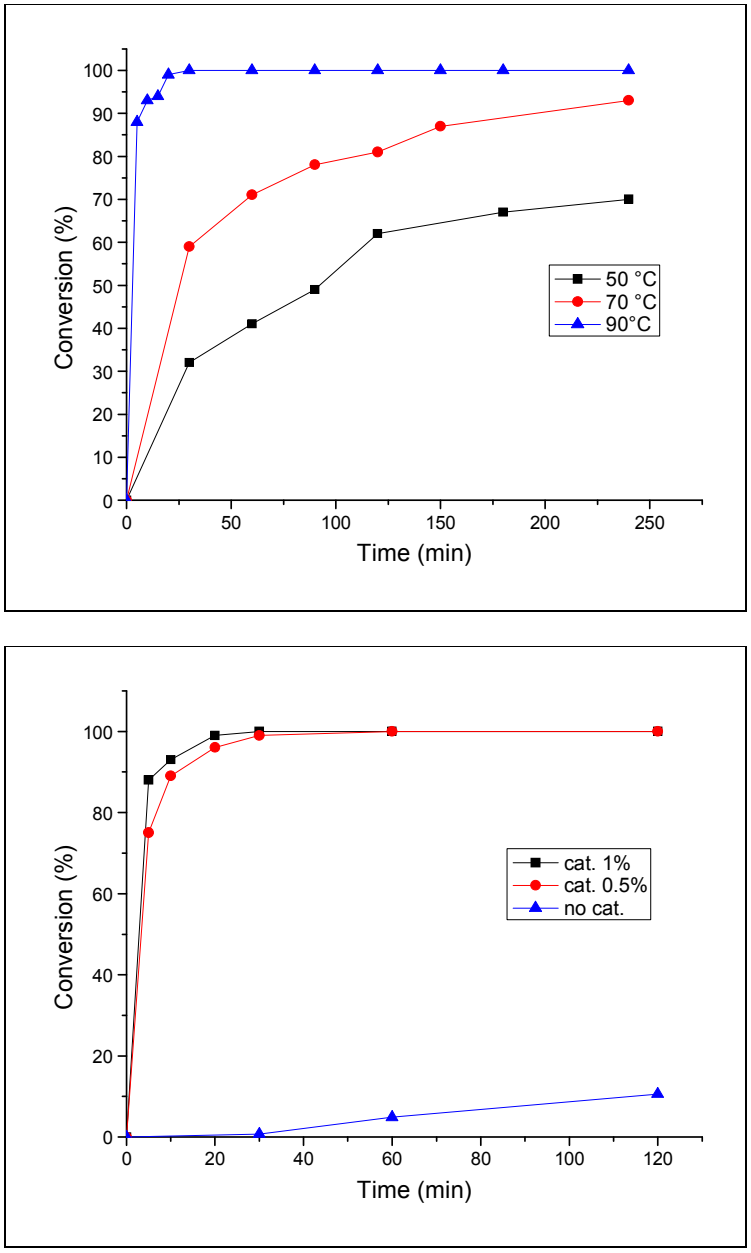


Figure 1. Conversion of 1,2-propanediol in the reaction with DMC catalyzed by $[P_{8,8,8,1}][OCO_2Me]$. Top: effect of the reaction temperature (molar ratio **2**:DMC:$[P_{8,8,8,1}][OCO_2Me]$=1: 20: 0.01, respectively). Bottom: effect of the catalyst amount (90 °C; molar ratio **2**:DMC=1: 20; $[P_{8,8,8,1}][OCO_2Me]$: 0 to 0.01 equivs with respect to **2**).

At 90 °C (boiling point of DMC), **1a** was a highly active catalyst: after 30 min, the conversion of 1,2-propanediol was quantitative even when the amount of the phosphonium salt was as low as 0.5 mol% (Figure 1: bottom, red profile). By contrast, the non-catalytic reaction was of no practical significance (bottom: blue profile). The decrease of the temperature from 90 to 50 °C produced a remarkable reduction of the conversion (figure 1, top); nonetheless, the selectivity towards propylene carbonate (**2a**) was always very good (> 95%).

Further experiments were carried out to evaluate possible effects of the DMC:**2** molar ratio. Based on the results of Figure 1, reactions were performed at 90 °C, in the presence of 0.5 mol% (with respect to **2**) of $[P_{8,8,8,1}][OCO_2Me]$ as the catalyst. Under such conditions, 1,2-propanediol (837 mg) was set to react with variable amounts of DMC: in particular, the DMC:**2** molar ratio was progressively decreased from 20 to 2. Results are reported in Figure 2 where the conversion profiles of **2** with time are shown at the different reactant molar ratios.

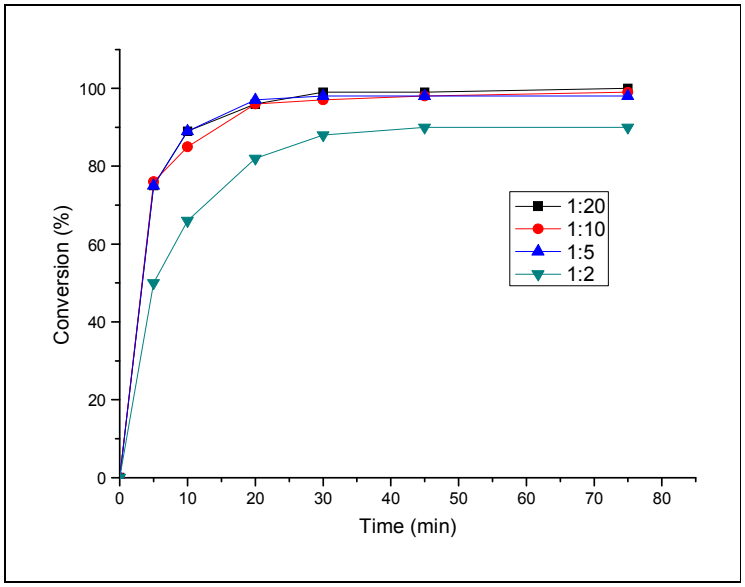


Figure 2. The reaction of 1,2-propanediol (**2**) with DMC catalyzed by $[P_{8,8,8,1}][OCO_2Me]$ (90 °C; molar ratio **2**:cat= 1:0.005). Effect of DMC:**2** molar ratioon the reaction conversion. For convenience, some results of Figure 1 (bottom) are also shown (black profile, DMC:**2**=20).

The reduction of the DMC:**2** molar ratio from 20 to 5 had no dramatic consequences on the reaction outcome: after 30 min, the conversion of 1,2-propanediol was quantitative in all cases

(black, red and blue profiles). When the DMC amount was further decreased (DMC:**2**=2), the diol conversion was still satisfactory (around 90 %); though, a remarkably slower reaction was observed (green profile). No appreciable changes were noted in the product distribution: propylene carbonate was always obtained with very high selectivity (up to 95%).

Under the conditions of Figure 2 (molar ratio DMC:**2**=5), catalyst recycle was also explored. Accordingly, the same catalytic sample was reused for three subsequent reactions of DMC and **2** at 90 °C for 60 min. Once the first experiment was complete, the excess of DMC and the co-product MeOH were removed by rotary evaporation. Next, propylene carbonate was recovered by distillation under vacuum (65 °C @ 200 Pa). To the residual catalyst **1a** was added a fresh aliquot (4.6 mL) of DMC and **2a** (in a 5:1 molar ratio, respectively). The mixture was then set to react at 90 °C for 60 min. The same reaction/catalyst reuse cycle was repeated a third time. The three tests showed an excellent reproducibility: in all cases, the conversion of **2** was 98-99% and the selectivity towards the formation of propylene carbonate was >95%. The stability and recyclability of the catalyst was thus confirmed.

Overall, the preliminary experiments proved that: i) the transesterification of DMC with 1,2-propanediol was efficiently catalyzed by $[P_{8,8,8,1}][OCO_2Me]$, and ii) notwithstanding the different conditions investigated, the cyclic carbonate **2a** was always the preferred, if not the exclusive, product; iii) a reaction intensification was possible. Particularly, the amount of DMC could be reduced from 20 to 5 molar equivs with respect to the limiting diol.

The behavior of 1,2-propanediol was further explored in the transesterification with both DMC and DEC catalyzed by methylcarbonate and bicarbonate phosphonium salts, **1a** and **1b**, respectively. Since DEC was expected to be less reactive than DMC,[10] transesterification processes were carried out under the most favorable conditions of previous experiments from Figures 1 and 2. Accordingly, a mixture of **2** (837 mg), dialkyl carbonate (either DMC or DEC) and the catalyst (either **1a** or **1b**) in a 1:20:0.005 molar ratio, respectively, was set to react at 90 °C. The results are reported in Table 1.

Experiments confirmed the previously observed trend for the product distribution: at complete conversion, all reactions were highly selective towards the formation of the cyclic propylene carbonate (**2a**). The product was distilled under reduced pressure (65 °C @ 200 Pa) and isolated in 86-92% yields (entries 1 and 3). Both carbonate onium salts proved to be effective transesterification catalysts: they showed a comparable activity when DMC was used (entries 1-2), while in the case of DEC, $[P_{8881}][OCOOCH_3]$ (**1a**) was more efficient than $[P_{8881}][OCOOH]$ (**1b**) (entries 3-4).

Table 1. The transesterification of DMC and DEC with 1,2-propanediol catalyzed by carbonate phosphonium salts[a]

Entry	Carbonate	Catalyst	Time (h)	Product 2a (%)	
				NMR [b]	Isolated[c]
1	DMC	$[P_{8881}][OCOOCH_3]$	0.5	99	92
2	DMC	$[P_{8881}][OCOOH]$	0.5	99	
3	DEC	$[P_{8881}][OCOOCH_3]$	3	95	86
4	DEC	$[P_{8881}][OCOOH]$	3	74	

[a]All reactions were carried out at 90 °C, using **2**, dialkyl carbonate (either DMC or DEC) and the phosphonium salt in a 1:20:0.005 molar ratio.[b] % Amount of propylene carbonate (**2a**) determined by ^{1}H NMR analyses; [c] Isolated yield of **2a**. Product was isolated from reactions scaled to 22 mmols.

The reproducible behaviour of transesterifications with DEC was further verified by four repeated reactions: two of them were run under the conditions of entry 3, and two others were performed under the conditions of entry 4 (Figure 3, black and red profiles, respectively).

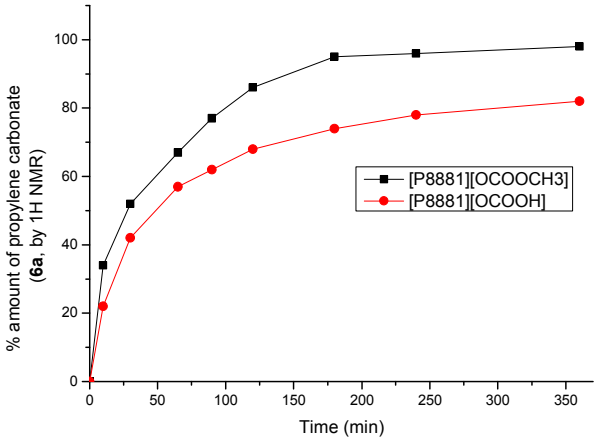


Figure 3. The formation of propylene carbonate during the transesterification of DEC with 1,2-propanediol catalyzed by $[P_{8881}][OCOOCH_3]$ (**1a**) and $[P_{8881}][OCOOH]$ (**1b**) (black and red profiles, respectively). In each profile, points indicated the average % amount of propylene carbonate (**2a**, by ^{1}H NMR analysis) measured in two reactions repeated under identical conditions. Experiments were highly reproducible: at the chosen time intervals, amounts of **2a** did not differ by more than 7% from each other.

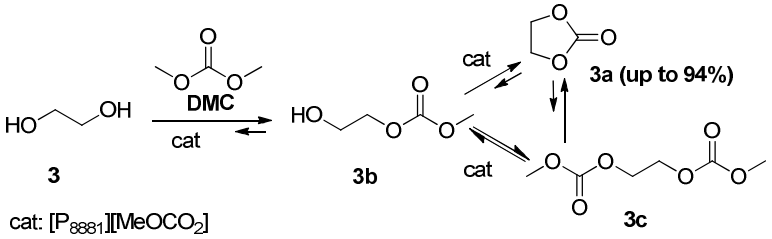
After 180 min, the formation of **2a** was 93% and 73% for the reaction catalysed by **1a** and **1b**, respectively. No clear reasons accounted for such a substantial difference: a similar effect was never observed in previous comparisons of salts **1a** and **1b** as organocatalysts for both transesterification processes and Michael- or Henry-type nucleophilic additions.[7-9]

In the presence of **1a** as a catalyst, the scale-up of the reaction of propylene glycol (**2**) to propylene carbonate with DMC was also investigated. A mixture of **2** (200 g, 2.63 moles), DMC (474 g, 5.26 moles; DMC:**2** = 2.00), and **1a** (6.48 g, 13.1 mmol; **1a**:**2** = 0.005) was set to react for 1 hour at the reflux temperature. Then, the MeOH/DMC azeotrope and the excess DMC were removed by rotary evaporation. Propylene carbonate **2a** was purified by distillation under vacuum (65 °C @ 200 Pa): the pure product was obtained in a 96 % (258 g).

1,2-Ethanediol (ethylene glycol). The transesterification of DMC with ethylene glycol (**3**) was examined under the conditions of Figure 2 previously reported for 1,2-propanediol. At 90 °C, a mixture of **3** (683 mg, 11 mmol), and $[P_{8,8,8,1}][OCO_2Me]$ in a 1: 0.005 molar ratio, was set to react with two different amounts of DMC (1.98 and 4.95 g; the molar ratio DMC:**3** being 2 and 5, respectively). All experiments were carried out for 4 hours.

Two further transesterification tests were also considered: in the first one, the co-product methanol was continuously distilled off throughout the experiment; in the second reaction, a higher temperature of 120 °C was used. This required a stainless-steel autoclave since the operating temperature was above the boiling point of DMC.

^{1}H NMR analyses of the reaction mixtures indicated the formation of the cyclic carbonate – ethylene carbonate (1,3-dioxolan-2-one, **3a**) – as the major product (up to 94%). In analogy to 1,2 propanediol (Scheme 4), the other minor compounds were, most probably, the corresponding mono- and di-transesterified derivatives (**3b** and **3c**, respectively) shown in Scheme 5.



Scheme 5. Transesterification of 1,2-ethanediol with DMC catalyzed by $[P_{8,8,8,1}][OCO_2Me]$.

The experimental results are reported in Table 2.

Table 2.Transesterification of 1,2-ethanediol with DMC [a]

Entry	DMC:3 (mol:mol)	T (°C)	Conversion[b] (%)	Products[b] (%)			3a (Y,%)[c]
				3a	3b	3c	
1	2	90	88	83	15	2	
2	5	90	95	74	19	7	
3[d]	2	90	100	94	3	2	86
4	2	120	100	88	12		

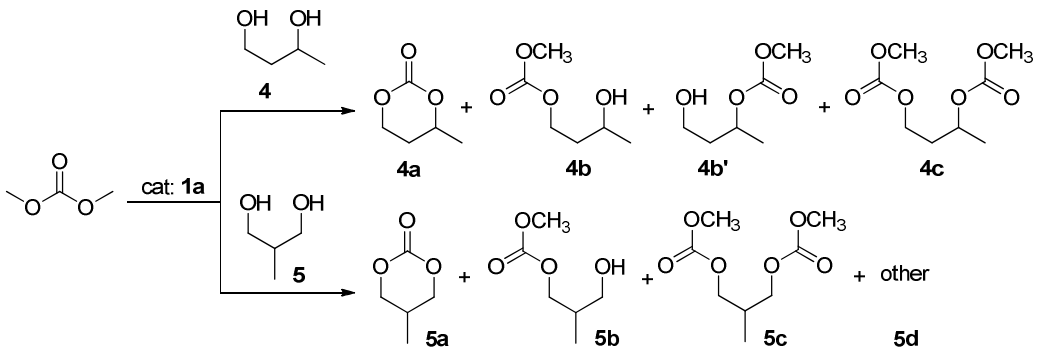
[a] All reactions were carried out in the presence of $[P_{8,8,8,1}][OCOOCH_3]$ as a catalyst (molar ratio **1a**:**3**= 0.005). [b]The reaction conversion and the product distribution were determined by ^{1}H NMR: reported values were obtained after 4 hours. [c] Isolated yield of the carbonate **3a**. Product was isolated from reactions scaled to 22 mmols. [d] A continuous distillation of the co-product methanol (at 70°C) was carried out.

In general, $[P_{8,8,8,1}][OCO_2Me]$ acted as an efficient catalyst also for the transesterification of DMC with ethylene glycol (**3**). Compound **3** however, was remarkably less reactive than 1,2-propanediol (**2**): under comparable conditions, the reaction of **2** was complete after 30 min, while the conversion of **3** was 95% after 4 hours (Figure 2, blue profile and Table 2, entry 2). Moreover, the amount of ethylene carbonate (**3a**) did not exceed 83% (entry 1), while propylene carbonate (**2a**) was obtained with a much higher selectivity (≥95%, Figure 2).

This trend was confirmed also by the reaction carried out at 120 °C: although the increase of the temperature allowed a quantitative conversion of **3**, the formation of the cyclic carbonate was only slightly improved (88%, entry 4).

Better results were achieved when the co-product methanol was continuously removed by distillation: this expedient allowed to boost the selectivity towards the formation of **3a** up to 94% (entry 3). Once the reaction was complete, product **3a** was distilled under vacuum (78 °C@200 Pa) and isolated in 86% yield.

1,3-Diols. 1,3-Butanediol (**4**) and 2-methyl-1,3-propanediol (**5**) were chosen as model compounds. Initial experiments were carried out under the conditions previously explored for 1,2-diols: a mixture of **4** or **5** (991 mg, 11 mmol), DMC (18.5 mL), and $[P_{8,8,8,1}][OCO_2Me]$ in a 1:20:0.005 molar ratio, respectively, was set to react at 90 °C, for 23 hours. At intervals, samples of such a mixture were withdrawn and analyzed by both ^1H NMR and GC/MS. In the reaction of compound **4**, four products were observed: the cyclic carbonate (4-methyl-1,3-dioxan-2-one, **4a**), the double-transesterification derivative (butane-1,3-diyl dimethyl dicarbonate, **4c**) and other two compounds most likely derived from mono-transesterification (3-hydroxybutyl methyl carbonate, 4-hydroxybutan-2-yl methyl carbonate, **4b**, **4b'**, respectively) (Scheme 6, top). Four products were detected also in the reaction of **5**: the corresponding cyclic carbonate (5-methyl-1,3-dioxan-2-one, **5a**), the mono- and di-carbonate derivatives [3-hydroxy-2-methylpropyl methyl carbonate and dimethyl (2-methylpropane-1,3-diyl) dicarbonate, **5b** and **5c**, respectively], and another unidentified compound (other **5d**) (Scheme 6, bottom).



Scheme 6. The transesterification of DMC with 1,3-butanediol (**4**) (top) and 2-Methyl 1,3-Propanediol (**5**) (bottom), catalyzed by **1a**.

Since compound **5b** formed in a reasonable amount (up to 20% at the beginning of the reaction), an additional transesterification reaction of DMC with **5** was carried out to isolate such product. The experiment was set up under the above described conditions and it was stopped after the first 10 minutes by quenching the reaction with aq. HCl. Compound **5b** could be purified by FCC, and isolated in a 12% yield. NMR analyses fully confirmed the structure of **5b** reported on Scheme 6.

Figure 4 illustrates the results achieved in the reaction of DMC with compounds **4** and **5**: the conversion of both diols and the corresponding product distributions are plotted as a function of time.

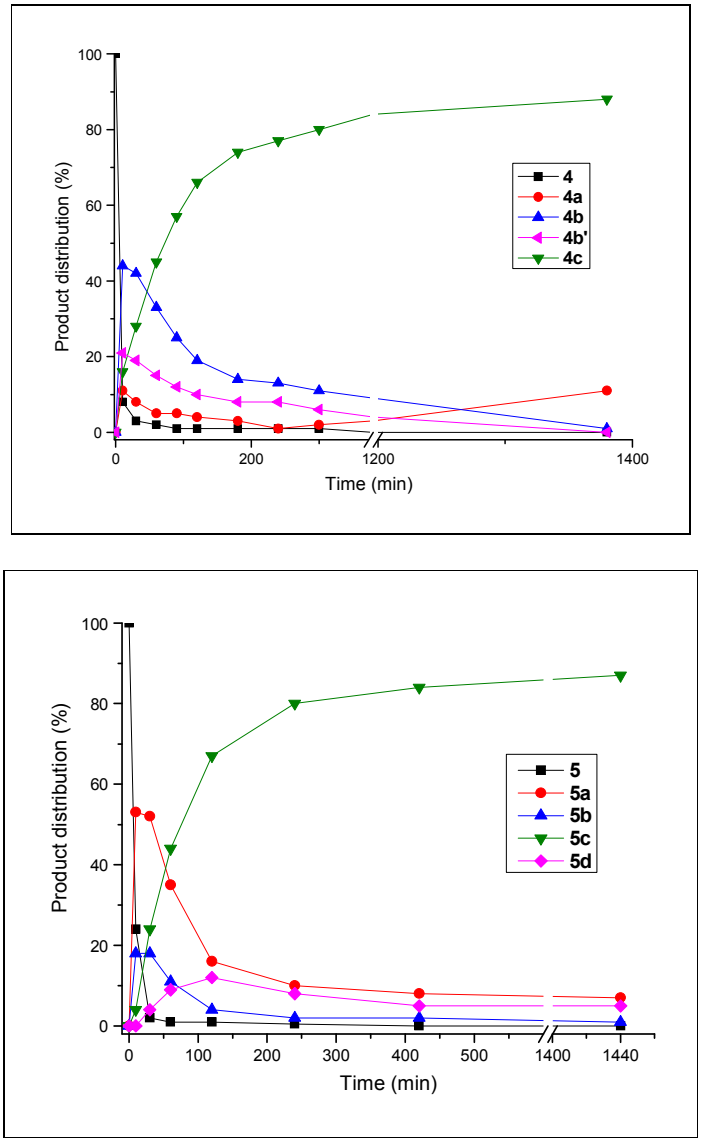


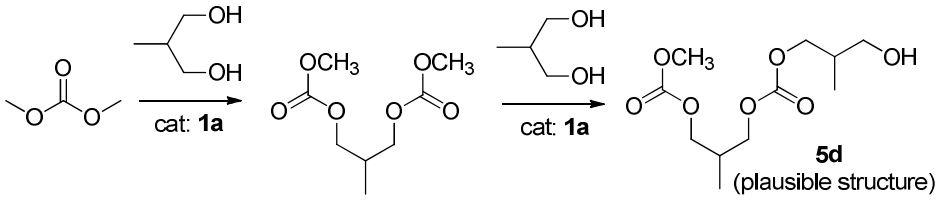
Figure 4.The product distribution observed for the reaction of DMC with 1,3-butanediol (**4**) (top); 2-methyl-1,3-propanediol (**5**) (bottom) (90 °C, molar ratio 1,3-diol:DMC:$[P_{8,8,8,1}][OCOOMe]$ = 1:20:0.005)

In the case of 1,3-butanediol (**4**) (Figure 4, top), the experiment showed that after the first hour, the conversion was substantially quantitative and a mixture of all products **4a-c** was obtained. As the reaction proceeded further, the amount of compounds **4a-b/b'** progressively decreased in favor of the formation of **4c** that reached ~90% after 23 hours (green profile). This result was confirmed by an additional experiment in which a mixture of 1,3-butanediol (0.99 g), DMC (18.5 mL), and **1a** (27 mg; amounts of reactants/catalyst and their relative molar ratio were those above described) was set to react in the presence of 4-clorotoluene (1.39 g) as an internal standard (IS). After 23 hours at 90 °C, the yield of **4c** based on the IS was 87%.

Product **4c** was recovered by vacuum distillation (70 °C@ 120 mbar) and isolated in a 72 % yield.

A similar behavior was displayed by the reaction of 2-methyl-1,3-propanediol (**5**) (Figure 4, bottom). Also in this case, after an initial formation of products **5a-d**, the reaction mixture reached an equilibrium composition in which the dicarbonate derivative **5c** was by far, the most abundant compound (85%, green profile); **5c** was distilled under vacuum (70 °C@100 Pa) and isolated in 75% yield.

The product **5d** was not identified; however, its spectroscopic (GC/MS) analysis and the bell-shaped profile of its formation (magenta curve, Figure 4, bottom) suggested a backbone compatible with a high molecular weight carbonate obtained via a reversible reaction.[11] A plausible structure for **5d** was then hypothesized via a multiple transesterification process of DMC with **5** (Scheme 7).



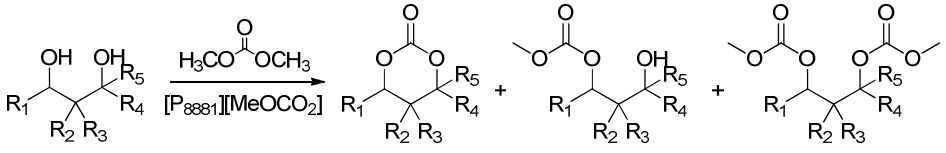
Scheme 7. Proposed structure for product **5d**.

Overall, the results of Figure 4 indicated that: i) the catalyst ($[P_{8,8,8,1}][OCOOCH_3]$) efficiently activated both the primary and secondary OH groups of **4** and **5** for the transesterification with DMC; ii) a striking difference was manifest between 1,3-diols (**4** and **5**) and 1,2-diols. Under

comparable reaction conditions, the former (**4** and **5**) preferentially gave linear dicarbonates **4c** and **5c**, while the latter (**2** and **3**) yielded the corresponding cyclic carbonates (**2a** and **3a**, respectively) with selectivity ≥ 95%. The selectivity towards linear products **4c** and **5c** was particularly noteworthy since such compounds, once formed, were expected to react further to give oligomers and finally, polycarbonates. The latter however, were never observed, not even in trace amounts.

This behavior was confirmed by additional experiments carried out with 1,3-butanediol, in which the molar ratio DMC:**4** was varied between 2 and 20 and the temperature was increased up to 120 °C (in a stainless-steel autoclave). $[P_{8,8,8,1}][OCO_2Me]$ was always used in 0.005 molar equivs. with respect to **4**. In all cases, the initial formation of mixtures of **4a-d** was followed by the progressive increase of the dicarbonate **4d** which was recovered in amounts ranging from 50 to 90% after 7 and 23 hours of reactions, respectively.

Other 1,3-diols such as 1,3-propanediol (**6**), 2,2-dimethyl 1,3-propanediol (**7**), and 2-methyl 2,4-pentandiol (**8**) were then used in the reaction with DMC. Conditions were those most frequently employed for the above described tests: accordingly, a mixture of the selected diol (**6**, **7** and **8**: 11 mmol; 0.84, 1.15, and 1.30 g, respectively), DMC (19.8 g, 220 mmol,), and $[P_{8,8,8,1}][OCO_2Me]$ in a 1:20:0.005 molar ratio, respectively, was set to react at 90 °C, for 12 hours. At intervals, samples of such a mixture were collected and analyzed by both ^1H NMR and GC/MS. In the case of compounds **6** and **7**, three products were observed: they were the corresponding cyclic carbonates (**6a** and **7a**), and the derivatives of mono- and double-transesterification of the reacting diol (**6b-6c**, and **7b-7c**, respectively) (Scheme 8). In the case of compound **8**, only the cyclic carbonate (**8a**) and the monocarbonate (**8b**) were detected (Scheme 8).



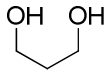
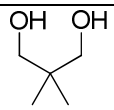
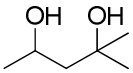
6-8 **6a-8a** **6b-8b** **6c-7c**

6: $R_1=R_2=R_3=R_4=R_5=$ H
7: $R_1=R_4=R_5=$ H; $R_2=R_3=CH_3$
8: $R_1=R_4=R_5=CH_3$; $R_2=R_3=$ H

Scheme 8. The transesterification of DMC with 1,3-propanediol (**6**), 2,2-dimethyl 1,3-propanediol (**7**), and 2-methyl 2,4-pentadiol (**8**), catalyzed by **1a**.

Results are reported in Table 3. For each substrate (**6-8**), the conversion and the product distribution are shown after 0.5 and 12 hours of reaction.

Table 3. The transesterification of DMC with 1,3-propanediol (**6**), 2,2-dimethyl 1,3-propanediol (**7**), and 2-methyl 2,4-pentadiol (**8**).[a]

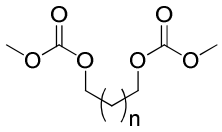
entry	1,3-Diol	Time (h)	Conv. (%)[b]	Products (%, NMR)[b]			Y (%)[c]
1	 **6**	0.5	93	**6a** 3	**6b** 51	**6c** 34	
2		12	>99	<1	11	89	85
3	 **7**	0.5	86	**7a** 19	**7b** 51	**7c** 12	
4		12	>99	1	18	81	70
5	 **8**	0.5	43	**8a** 21	**8b** 22	- -	
6		12	>99	96	3	-	95

[a] All reactions were carried out at 90 °C, using a mixture of 1,3-diol, DMC, and $[P_{8,8,8,1}][OCO_2Me]$in a 1:20:0.005 molar ratio, respectively. [b] The reaction conversion and the product distribution were determined by ^{1}H NMR. [c] Isolated yields of carbonates **6c**, **7c**, and **8a**, respectively. Products were isolated from a reaction scaled to 22 mmols.

The behavior of diols **6** and **7** paralleled the one of compounds **4** and **5**: once the equilibrium was reached, the corresponding linear dicarbonates **6c** and **7c** were obtained as major products in amounts >80% (entries 2 and 4). Both **6c** and **7c** were recovered by vacuum distillation and isolated in 85 and 70% yields, respectively.

A different outcome was observed for 2-methyl 2,4-pentandiol (**8**). In this case, the formation of the cyclic carbonate was highly favored: after 12 hours, compound **8a** was the sole reaction product (96%, entry 6). This was purified by sublimation under reduced pressure (~100 °C@200 Pa), and isolated in a 95% yield. Notably, the experiment proved that during the reaction: i) only one of the two expected monocarbonate derivatives was observed. A ^{13}C NMR analysis (see ESI for details) confirmed the presence of product **8b** resulting from the exclusive transesterification of DMC with the secondary hydroxyl group of **8** (@ C4). The tertiary OH function(@ C2) was totally unreactive; ii) not even trace amounts of the dicarbonate derivative were detected.

Other 1,n-diols. To conclude the investigation, the reactions of DMC with 1,4-butanediol (**9**) and 1,6-hexanediol (**10**) were explored. Experiments were carried out at 90 °C, using a mixture of the diol (**9** or **10**: 1.0 or 1.3 g, 11mmol), DMC (19.8 g, 220 mmol), and $[P_{8,8,8,1}][OCO_2Me]$ in a 1:20:0.005 molar ratio, respectively. Under such conditions, both primary hydroxyl groups of **9** and **10** underwent an exhaustive transesterification that gave the corresponding linear dicarbonates (Scheme 9: **9c** and **10c**, respectively): after 12 hours of reaction, these products were purified by distillation and isolated in 72% and 78% yields, respectively. Not even traces of oligomers or polycarbonates were detected.



9c: n = 2
10c: n = 4

Scheme 9. Dicarbonate products from the transesterification of DMC with 1,4-butanediol (**9**) and 1,6-hexanediol (**10**)

DISCUSSION

Effect of diol structure. The analysis of the investigated transesterification reactions proves that the structure and the relative OH-positions of the diols affect both the reaction conversion and the product distribution. Three aspects summarize the most salient results obtained so far with dimethyl carbonate: i) for 1,2-diols, the main products are cyclic C5-carbonates with yields and selectivity up to 96% and >99%, respectively. Ethylene glycol however, is definitely less reactive than 1,2-propanediol (Figure 2 and Table 2); ii) for 1,3-diols (**4-7**), although reactions are slower with respect to 1,2-diols, they afford linear dicarbonates **4c-7c** as preferential, if not exclusive, products once the equilibrium is reached (Figure 4 and Table 3). It should be noted that to date, a high yielding procedure for the syntheses of such linear derivatives is not described elsewhere via transesterification methods because the competitive formation of polycarbonates occurs preferentially over classical base-catalysts (see also below). A particular case is represented by 2-methyl-2,4-pentandiol (**8**) that possesses a tertiary OH group, the reaction of which with DMC does

not occur; notwithstanding this, the occurrence of an exhaustive transesterification process involving both hydroxyl functions of **8** is substantiated by the formation of the cyclic C6-carbonate **8a** (95%, Table 3); iii) for 1,n-diols (**9** and **10**), only linear dicarbonates **9c** and **10c** are obtained with not even trace amounts of cyclic derivatives. Polycarbonate formation is never observed.

A literature survey may offer different starting points to discuss such results. For one thing, the formation of cyclic carbonates *vs* linear products should be considered. Although Baldwin rules would predict that n-exo-trig type ring-closing processes (such as those involved for C5- and C6-cyclic carbonates) are favoured,[12] it has been often observed that exo double bonds in cyclic products tend to favour 5-membered rings more than 6-membered rings.[13] Specifically, for carbonate derivatives, the comparison of the chemical reactivity of C5- and C6-cyclic carbonates leaves few doubts on the higher stability of the former (C5) compounds.[13a, 13c, 14] This behavior has been rationalized through thermochemical and computional data as well as by measures of activation energies which support and predict a larger ring strain for C6-cycles with respect to C5-rings. Conformational effects due to the interactions between lone pairs of carbonate oxygen atoms and ring methylene hydrogens have been postulated: these (effects) should not have consequences in quasi-planar 5-rings, but they would produce 6-ring chair structures with unfavorable energies. Whatever the reason, the thermodynamic stability may also substantiate our evidence for the preferred formation of C5-cyclic carbonates with respect to the corresponding C6-derivatives. Moreover, the intramolecular nature of cyclization processes plausibly accounts for the favorable kinetic of C5-ring closing reactions (Figure 2) over the double (bimolecular) transesterification reactions necessary for linear dicarbonates **4c**-**7c**, and **9c**-**10c**, respectively (Figure 4).

There are however two manifest discrepancies between our results and literature reports. The first one pertains to the presence of alkyl substituents in the carbon chain of the diol. According to different authors,[13b,15] when these substituents are located on alkyl chains tethering two reacting (hydroxyl) centers of a diol, intramolecular transesterification reactions are facilitated and small carbonate rings are obtained. These observations are often described within the many variations

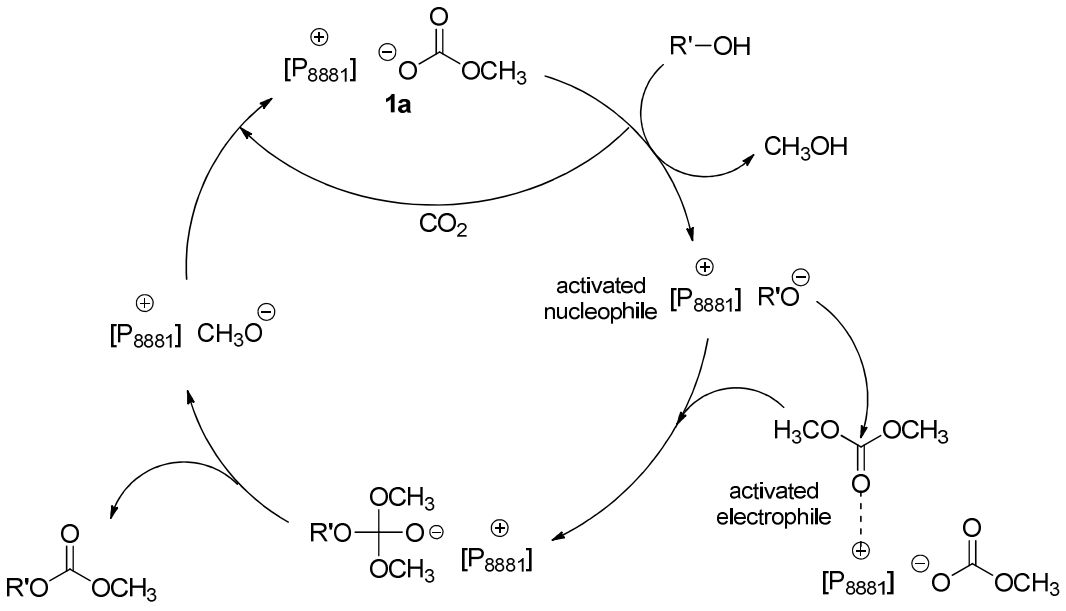
proposed for the so called "gem-disubstituent effect": the concept - originally formulated by Thorpe and Ingold[16] has been reviewed in 2005 by Jung and Piizzi,[17] that offered an analysis of fascinating early and recent theories based on the mutual repulsion of substituents (valency deviation), and the effect of reactive rotamers. In our case, although such notions may explain the easier formation of propylene carbonate with respect to ethylene carbonate (Figure 2), they hardly apply to account for the results of Table 3 and Figure 4. Except for 2-methyl 2,4-pentandiol (**8**), the investigated diols (**4**-**7**) produce the corresponding linear dicarbonates **4c**-**7c**: in other words, in our case methyl substituents located on the alkyl chains do not favor cyclic products at all.

The second question concerns the formation of polycarbonates. The literature well describes that in the presence of conventional organic and inorganic bases (amines, alcoxides, hydroxides, etc.) as catalysts, the transesterification of diols with light dialkyl carbonates (both DMC and DEC) suffers from the competitive formation of the corresponding polycarbonates.[3d, 14b,18] In general, the reaction of 1,X-diols with X= 3 affords mostly mixtures of cyclic molecules and polymers, while with X≥4, polycarbonates are the almost exclusive products. By contrast, our results (Figure 4, Table 3, and Scheme 9) show that linear dicarbonates **4c**-**7c** and **9c**-**10c** are obtained, without any trace of polymers even in the case of 1,4-butanediol and 1,6-hexanediol (**9** and**10**, respectively).

To complete the picture, two very recent reports should be here mentioned. In the first one,[19] the reaction of 1,4-diols with DMC and NaOMe as a catalyst, has been described under conditions by which five-membered cyclic ethers are the final products. However, not even traces of such derivatives (particularly of tetrahydrofuran) were detected by us during the reaction of 1,4-butanediol catalyzed by **1a**. In the second paper, the selective formation of linear dicarbonates (including some compounds of Schemes 6-8 and Table 3) from 1,3-diols and DMC has been achieved only under biocatalytic conditions, in the presence of a lipase enzyme.[20]

In our case, the observed behavior finds a plausible explanation in the nature of the organocatalysts used for the transesterification processes.

The role of carbonate phosphonium salts as catalysts. As was mentioned in the introduction, phosphonium ionic liquids such as salts **1a** and **1b**, are excellent catalysts not only for transesterification processes, but also for several C-C bond forming reactions.[7-9] Of particular note is the fact that although these salts possess poorly basic anions (*i.e.*methylcarbonate and carbonate), their performance is comparable to that of organic superbases. This behavior has been explained through the concept of ambiphilic (both nucleophilic and electrophilic) catalysis by which ILs act as catalysts via ion pairs.[7,8c,21] In particular, our previous investigation on model transesterification reactions of primary and secondary alcohols with dialkyl carbonates,[7] highlighted two effects: i) an electrophilic activation due to the coordination of the phosphorous center of the catalyst (as a Lewis acid) to the basic carboxylic oxygen of dialkylcarbonates; ii) a nucleophilic activation due to an acid-base reaction between the alcohol and the basic anion of the catalyst (Scheme 10).



Scheme 10. Ambiphilic catalysis for transesterification reactions in the presence of carbonate phosphonium salts [the model case of methyl trioctylphosphonium methyl carbonate (**1a**) is shown].

The first equilibrium of scheme 10 is to the left, however once the activated nucleophilic alcoxide $[P_{8881}][R'O]$ forms, it is immediately captured by DMC that is electrophilically activated by a second molecule of catalyst, driving the reaction forward. The electrophile and the nucleophile,

triggered by the catalyst, react according to the usual pattern of nucleophilic acyl substitutions (NAcS) to yield the transesterification product CH_3OCO_2R' and restore the initial ionic liquid **1a** by incorporating CO_2 back into the anion.

A further support to this mechanistic hypothesis comes also from an additional experiment in which an equimolar mixture of salt **1a** (500 mg) and 1,2-propanediol (77 mg) has been set to react at 90 °C for 21 hours. Under such conditions, NMR analyses have proved that the catalyst structure does not change and not even traces of the cyclic carbonate **2a** are formed. In short, the methylcarbonate anion of the catalyst does not possess any carbonylating activity.

The large steric bulk of the phosphonium compared to the reactants accounts for two other facts already described by us:[7] i) the exclusive formation of mono-transesterification products ($ROCO_2R'$). With respect to DMC (or DEC), once bulkier mono-transesterification derivatives are obtained, any catalytic activation and reaction are inhibited; ii) the higher reactivity of primary OH groups with respect to secondary ones. The effect of the progressive crowding at the OH functions becomes so relevant that for tertiary alcohols, the corresponding transesterification reaction is no longer possible over ILs catalysts.

This analysis may offer a basis to discuss the product distribution observed for the transesterification of DMC with diols **4-10**. In this case, the influence of the steric bulk of the reactants on their activation by onium salts (Scheme 10) as well as the non-favorable energetics of C6-ring closing (see above) should be considered: the two effects plausibly contribute to drive the reaction towards mono-transesterification products (linear dicarbonates **4c**-**7c** and **9c**-**10c**), and to preserve these compounds from further reactions that would yield polycarbonates. Figuratively, the large phosphonium carbonate ion pair mimics the active binding site of an enzyme: the synergic catalytic effect of the cation and anion of the salt results in a high reaction rate even when a very low catalyst loading is used, and an unusual selectivity compared to other more conventional catalysts.

The cooperative catalysis mechanism may also help to discuss the selective formation of the cyclic carbonate (**8a**) from 2-methyl 2,4-pentandiol (**8**) (entries 5-6, Table 3). A hypothesis is that the (difficult) approach/coexistence of sterically encumbered sites on both the diol **8** and the intermediate monocarbonate **8b** along with a modest nucleophilic activation of the tertiary OH group, favors an intramolecular transesterification reaction of **8b** which affords the cyclic derivative **8a** as the preferred product.

Finally, it should be noted that all the intermediate steps of scheme 10 are equilibrium reactions. This implies that in the end the preferred products will be the thermodynamically more stable ones. While, for example, substituted diol **7** appears to form cyclised **7a** more rapidly than does diol **6** (table 3, lines 1-4), probably because **7a** is kinetically more favoured than **6a**, nonetheless if the reaction is brought to completion the main observed product in both cases was the linear dicarbonate.

Different dialkyl carbonates and catalysts. The results of Table 1 indicate that the synthetic scope of the procedure may be extended to different dialkyl carbonates of which DMC and DEC are model examples. In the presence of 1,2-propanediol, the lower reaction rate observed for DEC with respect to DMC, parallels a trend already reported in comparative kinetic analyses of several other alkylations and carboxyalkylations mediated by organic carbonates:[10] the heavier the (dialkyl) carbonate, the poorer its reactivity. In the specific case of the transesterification process, both the leaving group ability of alkoxide anions (RO) and the accessibility of nucleophiles to the carbonyl carbon of dialkyl carbonates are plausibly disfavored when DMC is replaced by DEC.

As far as salts **1a** and **1b**, it is not surprising that their very similar structures may allow comparable catalytic performances. This behaviour has been observed by us in previous applications of such catalysts,[7-9] and it is confirmed by the results of Table 1 when reactions of DMC are considered (entries 1-2, Table 1). By contrast, the minor activity shown by **1b** in the reaction of DEC (Table 1, entry 4; Figure 3), has presently no clear reasons.

Conclusions

This investigation proposes a high-yielding procedure for the synthesis of both C5-cyclic carbonates and linear dicarbonates such as compounds **4c**-**7c** and **9c**-**10c**. In addition, it offers food-for-thought on the parameters that control product distribution during the transesterification of dialkyl carbonates with diols. In this respect, the structure of diols as well as the nature of the organocatalysts play a critical role. The preference for ring closing reactions shown by 1,2-diols is most plausibly due to the greater stability of C5-membered cycles. Instead, the (preferred) occurrence of bimolecular processes for 1,n-diols (n ≥3) can be ascribed to two effects: on one hand, the less favorable energetics of C6-ring closing processes, on the other, the influence of the steric bulk of the reactants on their activation by the catalytic onium salts, that derives from a cooperative catalysis mechanism.

This last observation further corroborates the choice of carbonate-exchanged phosphonium salts as catalysts for this study: since compounds **1a** and **1b** operate through a cooperative nucleophilic – electrophilic activation of the reagents and since they are effective for primary and secondary OH groups, therefore they may be used as a powerful tool to tune the access to cyclic or linear products, and to prevent polycarbonate formation. It should be noted that linear dicarbonates are not otherwise accessible in good yields by other conventional base catalyzed methods.

A final mention goes to the green features of the procedure that makes use of: i) non-toxic dialkyl carbonates, particularly DMC, for both the synthesis of ILs catalysts and the transesterification step, and ii) stable and recyclable catalysts that are so efficient to be used in amounts as low as 0.5 mol% (with respect to the limiting diols).

EXPERIMENTAL SECTION

1,2-propanediol (**2**), 1,2-ethanediol (**3**),1,3-butanediol (**4**), 2-methyl-1,3-propanediol (**5**), 1,3-propanediol (**6**), 2,2-dimethyl-1,3-propanediol(**7**), and 2-methyl-2,4-pentandiol (**8**), 1,4-butanediol (**9**) and 1,6-hexanediol (**10**), dimethyl carbonate (DMC), methanol, propylene and ethylene

carbonate were ACS grade and were employed without any further purification. Phosphonium salts **1a** and **1b** were prepared accordingly to a method recently reported by us.[8b]

GC/MS (EI, 70 eV) analyses were run using a HP5-MS capillary column (30 m). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra at 101 MHz. Chemical shifts were reported in δ values downfield from TMS; $CDCl_3$was used as solvent. IR spectra were recorded using NaCl windows. Combustion analysis data were obtained by an organic (CHN) elemental analyzer.

Structures of final products, both cyclic and linear dicarbonates, as well as those of reaction intermediates were analyzed byGC-MS and NMR techniques. Whenever characterization data were available in the literature, they were in agreement with our spectroscopic results and confirmed the assigned structures.[19,20,22,23]In the case of propylene and ethylene carbonate (**2a** and **3a**), structures were proved also by comparison to authentic commercial samples.

Transesterification reactions

1,2-propanediol. A typical procedure is described for the model case of 1,2-propanediol (**2**). A round-bottomed 25-mL flask equipped with a condenser and a screw-capped adapter for the withdrawal of samples, was charged with a mixture of 1,2-propanediol (0.84 g,11 mmol), dimethyl carbonate (DMC) (19.8 g, 220 mmol) and $[P_{8,8,8,1}][MeOCOO]$ **1a** (0.056 g,0.11 mmol). The flask was heated at the reflux temperature (90°C) in an oil bath, and the mixture was allowed to react under magnetical stirring, for 4 hours. The progress of the reaction was monitored by sampling the mixture at chosen time intervals, and by analyzing samples *via* NMR.

The above described procedure was used also to investigate the effect of the reaction temperature, of the catalyst loading, and of the DMC amount In particular: i) two experiments were carried out at 70 and 50 °C, respectively; ii) two experiments were carried out at 90 °C, for 2 hours, in the presence of variable amounts of the catalysts **1a** (0.11 mmol and 0.055 mmol: 0.056 and 0.027 g, respectively). An additional test was also performed in the absence of the catalyst; iii)four experiments were carried out at 90 °C, for 2 hours, in the presence of variable amounts of DMC (220, 110, 55 and 22 mmol; 18.54, 9.27, 4.63 and 1.85 mL, respectively).

The above described procedure was used also to investigate the recycle of the catalyst. Two recycling tests were performed. A first experiment was carried out at 90 °C, using a mixture of 1,2-propanediol (0.84 g,11 mmol), dimethyl carbonate (DMC) (4.75 g, 55mmol) and fresh $[P_{8,8,8,1}][MeOCOO]$ (**1a**: 0.027 g,0.055mmol). Once the reaction was complete (2 hours), the excess of DMC and the co-product MeOH were removed by rotary evaporation. Then, propylene carbonate was distilled under vacuum (65 °C@200 Pa). To the residual catalyst **1a** was added a fresh aliquot of DMC (4.75 g) and **2a** (0.84 g). The mixture was then set to react at 90 °C for 2 hours. After the completion of the second reaction, and the subsequent removal of the DMC, MeOH and propylene carbonate, the procedure was repeated once again.

The above described procedure was used also to investigate transesterification reactions with diethyl carbonate (DEC)and with $[P_{8,8,8,1}][HOCOO]$ (**1b**) as the catalyst. In particular: i) diethylcarbonate (DEC) (26 g, 220 mmol) was used in place of DMC; ii) $[P_{8,8,8,1}][HOCOO]$ (**1b**: 0.025 g, 0.055 mmol) was used in place of $[P_{8,8,8,1}][MeOCOO]$ (**1a**). All the other conditions were kept unaltered.

The transesterification of DMC with 1,2-propanediolwas scaled up according to the following procedure. A 1L-jacketed reactor equipped with a mechanical stirrer and a reflux condenser, was charged with 1,2-propanediol **2** (200 g, 2.63 moles), DMC (475 g, 5.28 moles), and $[P_{8,8,8,1}][MeOCOO]$ (**1a**: 6.47 g 13.2 mmoles). The mixture was stirred and heated at the reflux temperature for 1 hour. A methanol/DMC azeotropic mixture (130 mL) was then distilled and the resulting pale yellow liquid was concentrated by rotary evaporation in order to remove the excess of DMC. The crude propylene carbonate **2a** was finally distilled at reduced pressure yielding 258 g of colourless liquid (96 %).

Ethanediol (3). The procedure above described for 1,2-propanediol was used also to investigate the transesterification of DMC with ethanediol (**3**). A mixture of ethanediol (11 mmol, 0.68 g), DMC (22 mmol or 55 mmol: 1.85 or 4.63 mL, respectively) and **1a** (0.055 mmol, 0.027 g) was set to react at 90 °C, under magnetical stirring, for 4 hours. An additional experiments was carried out

by continuously removing the co-product methanol from the reactant mixture: this was done by heating the condenser (on top of the flask) at a constant temperature of 70 °C.

The reaction of DMC and ethanediol was also examined at a higher temperature of 120 °C. In this case, a mixture of **3** (11 mmol, 0.68 g), DMC (22 mmol, 1.85 mL) and **1a** (0.055 mmol, 0.027 g) was charged in a stainless steel autoclave (internal volume = 12 mL) equipped with a pressure gauge, a thermocouple for the temperature control, and a magnetic stirring bar. The autoclave was initially purged with nitrogen, closed, and finally heated electrically at the desired temperature for 4 hours.

1,3-Butanediol (4). Procedures above-described for reactions at both the reflux temperature and at 120 °C (autoclave) were used to investigate the tranesterification of DMC with 1,3-Butanediol (**4**). A mixture of 1,3-butanediol **4** (11 mmol, 0.99 g), DMC (55 or 220 mmol: 4.63 or 18.5 mL, respectively) and **1a** (0.055 mmol, 0.027 g) was used.

*Other 1,3-diols (**5-8**) and 1,n-diols (**9,10**).* The procedure above described for 1,2-propanediol was used to investigate also the transesterification of DMC with diols**5-10**. A mixture of the chosen diol (11 mmol), DMC (220 mmol, 19.8 g), and **1a** (0.055 mmol, 0.027 g) was set to react at 90°C in all cases.

Isolation and characterization of products

The most abundant products of the investigated transesterification reactions, in particular cyclic carbonates **2a**, **3a**, and **8a**, and linear dicarbonates **4c**, **5c**, **6c**, **7c**, **9c**, and **10c**, were isolated and fully characterized by MS and NMR. Also, two model mono-carbonate derivatives such as **5b** and **8b**, were isolated and characterized by NMR.

4-Methyl-1,3-dioxolan-2-one. Propylene carbonate (**2a**) was purified by distillation (65 °C@200 Pa) after reactions carried out under the conditions of entries 1 and 3 in Table 1. The corresponding yield were 92 and 86%, respectively. GC-purity was > 99% (colourless liquid). Mass spectrum (70 eV), m/z: 102 (M^+, 8%), 87 (30), 58 (16), 57 (100). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.90-4.80

(m, 1H); 4.55 (dd, J_1 = 8.3, J_2 = 7.8 Hz, 1H); 4.02 (dd, , J_1 = 8.4,J_2 7.2 Hz, 1H); 1.49 (d, J = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 154.9, 73.4, 70.7, 19.5.

1,3-Dioxolan-2-one. Ethylene carbonate (**3a**) was purified by distillation at reduced pressure (78 °C@200 Pa) after the reaction carried out under the conditions of entry 3 in Table 2. The isolated yield was 85%. GC-purity was > 99% (colourless liquid, solidified on standing at rt). Mass spectrum (70 eV), m/z: 88 (M^+, 100%), 73(2), 58 (10). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.5 (s, 4H).

Butane-1,3-diyl dimethyl dicarbonate.[20] The product (**4c**) was purified by distillation at reduced pressure isolated (70 °C@ 120 Pa) after the reaction carried out under the conditions of Figure 4 (top). The isolated yield was 72%. GC-purity was > 99% (colourless liquid). Mass spectrum (70 eV), m/z: 206 (M^+<1%), 162 (15), 135 (7), 131 (8), 130 (11), 115 (21), 104 (32), 103 (29), 98 (5), 91 (80), 87 (7), 85 (6), 77 (50), 72 (5), 71 (68), 59 (100), 57 (7), 56 (7), 55 (66), 54 (17). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.94-4.84 (m, 1H), 4.21 (t, J = 6.3 Hz, 2H), 3.78 (s+s, 6H), 2.05-1.87 (m, 2H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 150.6, 150.1, 67.0, 59.2, 49.6, 49.4, 30.0, 14.9.

2-Methyl propane-1,3-diyl dimethyl dicarbonate. The product (**5c**) was purified by distillation at reduced pressure isolated (70 °C@ 100 Pa) after the reaction carried out under the conditions of Figure 4 (bottom). The isolated yield was 75%. GC-purity was > 99% (colourless liquid). Mass spectrum (70 eV), m/z: 206 (M^+<1%), 135 (3), 130 (8), 117 (5), 102 (1), 98 (4), 91 (23), 87 (5), 86 (4), 85 (3), 77 (19), 73 (3), 72 (6), 71 (100), 59 (60), 57 (4), 56 (4), 55 (35), 54 (14), 47 (11), 45 (47), 43 (11), 42 (20), 41 (29), 39 (13). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.11-4.08 (m, 4H), 3.78 (s, 6H), 2.31-2.16 (m, 1H), 1.02 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.5, 68.8, 54.5, 32.4, 13.2. Anal. Calcd. for $C_8H_{14}O_6$: C, 46.60; H, 6.84. Found: C, 46.55; H, 6.87.

3-Hydroxy-2-methylpropyl methyl carbonate. The product (**5b**) was obtained by the following procedure. A mixture of **5** (991 mg, 11 mmol), DMC (18.5 mL), and $[P_{8,8,8,1}][OCO_2Me]$ in a

1:20:0.005 molar ratio, respectively, was set to react at 90 °C, for 10 min. Then, aq. HCl (5%, 1 mL) was added. DMC and methanol were removed at reduced pressure. The resulting oily mixture was subjected to FCC on silica gel (eluant: diethyl ether). The title compound (**5b**) was so isolated as a colorless liquid (12%). Mass spectrum (70 eV), m/z: 148 (M^+<1%) 77 (100%), 73 (4), 72 (8), 71 (13), 59 (21), 57 (24), 55 (17), 45 (19), 43 (19), 42 (35), 41 (31), 40 (4), 39 (16). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.22-4.06 (m, 2H), 3.78 (s, 3H), 3.63-3.48 (m, 2H), 2.10-1.97 (m, 1H), 0.97 (d, J = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 156.1, 69.8, 64.1, 54.7, 35.4, 13.4. Anal. Calcd. for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.59; H, 8.20.

Propane-1,3-diyl dimethyl dicarbonate.[22] The product (**6c**) was purified by distillation at reduced pressure (80 °C@200 Pa) after the reaction carried out under the conditions of entry 2 in Table 3. The isolated yield was 85%. GC-purity was > 99% (colourless liquid). Mass spectrum (70 eV), m/z: 192 (M^+<1%) 135 (3), 117 (11), 116 (14), 103 (6), 91 (51), 77 (21), 73 (16), 72 (50), 71 (34), 59 (100), 58 (4), 57 (46),55 (3), 47 (15), 45 (86), 44 (4), 43 (12), 42 (21), 41 (47), 39 (10). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.24 (t, J = 6.2 Hz, 4H), 3.78 (s, 6H), 2.04 (p, J = 6.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.4, 64.0, 54.5, 27.8.

2,2-Dimethyl propane-1,3-diyl dimethyldicarbonate. The product (**7c**) was purified by distillation at reduced pressure (68 °C@200 Pa) after the reaction carried out under the conditions of entry 4 in Table 3. The isolated yield was 70%. GC-purity was > 99% (colourless liquid). Mass spectrum (70 eV), m/z: 220 (M^+<1%), 135 (3), 132 (6), 131 (84), 91 (9), 87 (44), 85 (25), 77 (14), 74 (4), 71 (11), 69 (51), 68 (64), 67 (6), 59 (68), 57 (6), 56 (22), 55 (100), 53 (5), 45 (38), 43 (10), 41 (35), 39 (12). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.97 (s, 4H), 3.78 (s, 6H), 1.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.5, 72.3, 54.6, 34.8, 21.2. Anal. Calcd. for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 49.15; H, 7.27.

4,4,6-Trimethyl-1,3-dioxan-2-one. The product (**8a**) was purified by sublimation at reduced pressure (~100 °C@200 Pa) after the reaction carried out under the conditions of entry 6 in Table 3. The isolated yield was 95%. GC-purity was > 99% (white solid). Mass spectrum (70 eV), m/z: 144

(M^+<1%), 87 (2), 86 (2), 85 (37), 83 (4), 69 (3), 67 (6), 59 (35), 58 (9), 57 (28), 56 (100), 55 (12), 53 (4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.63 (dqd, J_1 = 12.4, J_2 = 6.2, J_3= 3.2 Hz, 1H), 1.85 (ddd, J_1 = 26.1, J_2 = 14.2, J_3 = 7.6 Hz, 2H); 1.46 (s, 6H); 1.41 (d, J = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 149.5, 80.9, 72.3, 40.5, 29.9, 26.5, 21.1. Anal. Calcd. for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.38; H, 8.44.

4-Hydroxy-4-methylpentan-2-yl methyl carbonate. The product (**8b**) was obtained by the following procedure. A mixture of **8** (11 mmol), DMC (18.5 mL), and $[P_{8,8,8,1}][OCO_2Me]$ in a 1:20:0.005 molar ratio, respectively, was set to react at 90 °C, for 10 min. Then, aq. HCl (5%, 1 mL) was added. DMC and methanol were removed at reduced pressure. The resulting oily mixture was subjected to FCC on silica gel (eluant: diethyl ether). The title compound (**8b**) was so isolated as a colorless liquid (10%). Mass spectrum (70 eV), m/z: 176 (M^+<1%), 119 (4), 85 (23), 83 (5), 77 (25), 67 (4), 59 (100), 58 (5), 57 (6), 55 (5), 45 (8), 43 (69), 42 (12), 41 (15). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.07-4.98 (m, 1H), 3.77 (s, 3H), 1.92 (dd, J = 15.0, 8.6 Hz, 1H), 1.65 (dd, J = 15.0, 3.4 Hz, 1H), 1.32 (d, J = 6.3 Hz, 3H), 1.25 (s, 3H), 1.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.3, 73.0, 69.8, 54.5, 48.8, 29.8, 29.7, 21.6. Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.58; H, 9.19.

Butane-1,4-diyl dimethyl dicarbonate.[19] The product (**9c**) was isolated at the end of a reaction carried out by using a mixture of **9** (11 mmol, 1.00 g), DMC (220 mmol, 18.5 mL), and **1a** (0.05 mmol, 0.027 g). Once the transesterification was complete (90 °C, 4 hours), the excess of DMC and the co-product methanol removed by rotary evaporation. The final product was then distilled at reduced pressure (65 °C@80 Pa). To avoid the solidification of the distillate, the condenser was kept at 50 °C throughout the distillation. The title compound **9c** quickly solidified on standing at rt. (72%, white solid; mp: 59-60°C). GC-purity was > 99%. Mass spectrum (70 eV), m/z: 206 (M^+<1%), 135 (14), 131 (5), 130 (8), 117 (19), 103 (4), 102 (66), 91 (42), 77 (41), 71 (31), 59 (73), 58 (28), 57 (4), 59 (73), 58 (28), 57 (4), 56 (4), 55 (63), 54 (100). ^{1}H NMR ($CDCl_3$, 400 MHz) δ

(ppm): 4.20-4.13 (m, 4H), 3.77 (s, 6H), 1.79-1.74 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.7, 67.3, 54.7, 25.1.

Hexane-1,6-diyl dimethyl dicarbonate. The product (**10c**) was isolated at the end of a reaction carried out by using a mixture of **10** (11 mmol, 1.30 g), DMC (220 mmol, 18.5 mL) and **1a** (0.05 mmol, 0.027 g). Once the transesterification was complete (90 °C, 4 hours), the excess of DMC and the co-product methanol removed by rotary evaporation. The final product was then distilled at reduced pressure (66 °C@80 Pa). To avoid the solidification of the distillate, the condenser was kept at 50 °C throughout the distillation. The title compound **10c** quickly solidified on standing at rt. (78%, white solid; mp: 50-51 °C). GC-purity was > 99%. Mass spectrum (70 eV), m/z: 234 (M^+<1%) 130 (2), 117 (5), 99 (4), 91 (9), 83 (35), 82 (100), 81 (11), 79 (3), 77 (34), 71 (11), 69 (5), 68 (6), 67 (82), 59 (32), 58 (4), 56 (4), 55 (45), 54 (67), 53 (4). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.13 (t, J = 6.6 Hz, 4H), 3.77 (s, 6H), 1.72-1.62 (m, 4H), 1.45-1.36 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.8, 67.9, 54.6, 28.5, 25.3. Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.31; H, 7.71.

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Electronic supplementary information (ESI section) including characterization data, NMR, IR and MS spectra of isolated compounds, is available.

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[11] Mass fragments of **5d** were highly compatible with the carbonate structure reported in Scheme 7 (details are in SI section). Though, the mass spectrum did not show the expected molecular ion (m/z = 264). This result matched the behavior of high-molecular weight dialkyl carbonates, the mass analysis of which rarely provide the corresponding molecular ions.

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